LIBRARY OF THE
UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

546
Il6i
1967/68

The person charging this material is responsible for its return on or before the **Latest Date** stamped below.

Theft, mutilation, and underlining of books are reasons for disciplinary action and may result in dismissal from the University.

University of Illinois Library

~~FEB 19 1971~~

L161—O-1096

I26i
1967/68

1 3

UNIVERSITY OF ILLINOIS

Inorganic Chemistry Seminar Abstracts

1967-1968

(October, 1967 thru May, 1968)

Page

Linkage Isomerism and Bonding in Complexes of Thiocyanate 1
Reactions of Lewis Bases with Boron Hydrides 7
Neutron Diffraction Studies of Magnetism in the Solid State 11
Studies of Some Cyclopentadienyl Compounds of the Representative Metals 15
Structure of Complex Ions in Molten Salts 18
The Kerr Effect 22
Approximate SCF Theories 26
Nuclear Magnetic Resonance Studies of Molecular Motion in Solids 30
Applications of Magnetic Circular Dichroism 35
Electrochemistry of Organometallic Compounds 38
Infrared Intensities of the CO Stretching Modes in Metal Carbonyls 42
The Possible Role of the Transition Metal in Certain Metallocene Substitution Reactions 45
The Synthesis, Characterization and Chemistry of C-Alkylamine Derivatives of $B_{10}CH_{13}^-$ and $B_{10}CH_{11}^-$. 49
Polarized Crystal Spectra of Transition Metal Complexes 52
Mechanism of Formation of Hydrogen Chromatophosphate(2-)[1] 57
Phosphorus (31) NMR 63
Magnetic Double Resonance 67
Tris Dithiolate Complexes--Trigonal Prismatic Coordination 71
Stereochemistry and Bonding in Eight Coordinate Complexes 75
Metal-Ligand Bonding in Substituted Metal Carbonyls 84
Experimental and Theoretical Studies of Inorganic Reactions 86
Association of Some Alkyllithium Compounds in Hydrocarbon Media as a Function of Added Lewis Bases 90
Electron Delocalization in Paramagnetic Nickel(II) - Ammine Complexes 92
Coordination of Molecular Nitrogen 95

UNIVERSITY OF ILLINOIS
JUL 31 1968
LIBRARY

LINKAGE ISOMERISM AND BONDING IN COMPLEXES OF THIOCYANATE

Sister M. M. Elsbernd October 10, 1967

Introduction

Linkage isomers are the isomeric forms of a coordination compound which can result whenever a given ligand can attach itself to the same central metal atom by bonding through either one of two or more different atoms within the ligand. The thiocyanate ion is such an ambidentate ligand since it can coordinate through the nitrogen or sulfur atom.

Current interest in this type of isomerism, particularly with the thiocyanate ion, comes from the observation by Turco and Pecile,[1] in 1961, that other ligands in the coordination sphere of a metal can influence the nature of the metal-thiocyanate bond. Two years later the first linkage isomers of thiocyanate were reported [2,3] and since then several more have been synthesized.[4-9]

Determination of the Bonding Mode

Thiocyanate ions form three types of complexes with a metal; namely, thiocyanato (M-SCN), isothiocyanato (M-NCS), and bridging (M-SCN-M) complexes. The different modes of bonding in these complexes can be differentiated by several methods.

The shift in the frequencies of the three fundamental modes of vibration in the thiocyanate ion upon complexation has been widely used to determine the bond type. For the free thiocyanate ion, as in KCNS, these frequencies are ν_1 = 743, ν_2 = 470 (doubly degenerate), and ν_3 = 2066 cm^{-1}.[10] (These modes of vibration are commonly designated as $\nu(CS)$, $\delta(NCS)$, and $\nu(CN)$ respectively.)

The C-N stretching frequencies of complex thiocyanates increase in the order: $CNS^- < M\text{-}NCS \leq M\text{-}SCN < M\text{-}SCN\text{-}M$.[11] A large increase in $\nu(CN)$ of 70-120 cm^{-1} relative to free thiocyanate ion is diagnostic of strongly bridged complexes.[12] For palladium complexes of the specific form $[PdL_2(CNS)_2]$, the values of the frequencies are indicative of the bond type: for M-SCN, $\nu(CN)$ is above 2100; for M-NCS, it is below or equal to 2100 cm^{-1}. [13] In general, the $\nu(CN)$ absorption is strong and exhibits a broad band for isothiocyanato complexes and a sharp band for thiocyanato complexes.

The infrared spectrum for the N-C-S bending mode in isothiocyanato complexes consists of a single band of medium intensity in the 460-490 cm^{-1} region, while in thiocyanato complexes, it consists of a medium band in the 410-440 cm^{-1} region with weaker satellites at higher values. [14] The C-S stretching frequency has often been considered diagnostic of the metal-ligand bond since $\nu(CS)$ is at 690-720 cm^{-1} for M-SCN and at 780-860 cm^{-1} for M-NCS complexes. [15] However, this frequency can be erroneously assigned since the absorption is of low intensity and the value of the first overtone of $\delta(NCS)$ of a thiocyanato complex falls in the $\nu(CS)$ region of an isothiocyanato compound.[13,16]

Digitized by the Internet Archive
in 2012 with funding from
University of Illinois Urbana-Champaign

http://archive.org/details/inorganicsemi196768univ

Kharitonov and co-workers have done a semi-empirical analysis of the vibrations of coordinated thiocyanate groups.[17] For isothiocyanato complexes, the observed increase of ν(CN) and ν(CS) with respect to the thiocyanate ion is caused by a change in the vibration mechanics of the system and not by a significant change in the force constants k_{CN} and k_{CS} upon coordination. For bridging complexes, the effects of both M-NCS and M-SCN bonding are present and are additive. These conclusions are in good agreement with those of Tramer,[12] who correlated variations in infrared spectra upon bonding with electronic changes in the thiocyanate group.

The types of coordination, M-SCN and M-NCS, can be differentiated also by the value of the integrated intensity A (M^{-1} cm^{-2}) of the ν(CN) absorption per single coordinated thiocyanate group: for M-SCN, A = 0.8-2.3 x 10^4; for M-NCS, A = 9-12 x 10^4.[18-20] The product ϵ_{max}x $\Delta\nu_{1/2}$ can be used in place of integrated intensity as a rough indication of the type of coordination.

Visible spectra can be used to differentiate bond types since the position of the thiocyanate ion in the spectrochemical series depends on the mode of coordination; i.e., $Br^- < Cl^- \approx -SCN^- < F^- < H_2O < -NCS^- < NH_3 < CN^-$.[21]

In addition to the above means, recent studies have indicated that changes in measured intensities in Raman spectra[22] and ^{14}N chemical shifts in soluble, diamagnetic complexes might be used to indicate bonding mode.[23]

Factors Affecting Mode of Bonding

The mode of metal-thiocyanate bonding is dependent upon the metal itself and the nature of the other ligands in the coordination sphere. In complexes in which thiocyanate is the only ligand, the metals of the first transition series, class (a) acceptors or hard metals, coordinate to the hard, nonpolarizable nitrogen end of the thiocyanate ion in accordance with the generalization that hard acids prefer hard bases.[24,25] Conversely, the soft, polarizable sulfur end binds more strongly to soft metals, or class (b) acceptors, which are the metals to the right of Group VII in the second and third transition series.

Jørgensen has suggested that for a given metal, the bond type may depend on the oxidation state of the metal.[26] The effective charge on the metal influences the nature of the metal-thiocyanate bond, as was shown by Wojcicki and Farona.[27] A decrease in charge on the metal from $[Mn(CO)_5SCN]$ to the isoelectronic $[Cr(CO)_5NCS]^-$ changes the bonding from M-SCN to M-NCS. The stabilizing nature of the metal-carbonyl π-bonding is invoked to explain this and similar results.[28]

Steric and electronic factors can alter the mode of the metal-thiocyanate bond when other ligands are introduced into the coordination sphere.[5,29-31] The steric requirements for the angular M-S-CN linkage are greater than for the linear M-N-CS bonding. Hence, a change to M-NCS bonding may occur when bulky ligands would create considerable steric strain with the otherwise expected M-SCN linkage, as in $[Pd(Et_4dien)NCS]^+$ compared with $[Pd(dien)SCN]^+$.[32]

Most of the electronic effects exerted by other ligands can be explained in terms of π-bonding.[1,13] Interaction of d-electrons on the metal with the

empty antibonding and empty d-orbitals localized on the sulfur atom results in additional stability for the M-S bond. Strong π-electron acceptors make the metal d-orbital electrons less available for bonding with the thiocyanate, thereby removing the source of additional stability for the M-S bond and enhancing a M-NCS linkage. Only very small effects may be required to alter the nature of thiocyanate bonding in some systems.[5,30] Frequently, steric and electronic effects are operative simultaneously and in the same direction.[29,32]

Kinetics and Mechanisms of Isomerization

Isomerization in inorganic linkage isomers of thiocyanate has not been studied extensively. In general, the rates are much greater in solution than in the solid state. Some specific rate constants, all of which are first order, have been determined as follows:

Compound	State	Temp., °C.	k, sec^{-1}	Reference
$[Cr(H_2O)_5SCN]^{+2}$	1.0M $HClO_4$	25	2.9×10^{-5}	8
$[Pd(Et_4dien)SCN]^{+}$	0.1M $NaClO_4$	20	2.6×10^{-4}	4
		35	1.05×10^{-3}	4
		45	2.56×10^{-3}	4
$[Rh(NH_3)_5SCN]^{+2}$	solid	78	2.7×10^{-6}	7
$[Pd(AsPh_3)_2(SCN)_2]$	KBr disk	126	3.47×10^{-5}	29

For the isomerization of $[Pd(Et_4dien)SCN]^{+}$, Basolo et al.[4] have proposed an intermolecular isomerization mechanism since the first-order rate constants for the isomerization and for the bromide substitution of the thiocyanate are the same and the substitution rate is independent of the bromide ion concentration. Haim and Stutin[8] have concluded that for the isomerization of $[Cr(H_2O)_5SCN]^{+2}$ an ion-pair mechanism is operative.

Properties of Known Isomers

The known linkage isomers of thiocyanate are given in Table 1, along with some of their properties. In most pairs of isomers, one complex is stable only at low temperatures and in the solid state. The equilibrium mixture of $[Mn(CO)_5CNS]$ isomers in solution is highly solvent dependent.[6] Linkage isomers in Cd^{+2}---CNS^{-} systems have been reported from several sources,[12,22,23] but the species present in these systems have been poorly characterized and the evidence appears inconclusive.

In addition to [Cu(tripyam)(NCS)(SCN)] given in Table 1, three other complexes have been reported to contain both N- and S-bonded thiocyanate: $[Pd(\emptyset_2As\emptyset P\emptyset_2)(NCS)(SCN)]$,[33] $[Pd(Me_2bipy)(NCS)(SCN)]$[5] and [Cu(tren)(NCS)(SCN)],[34] but X-ray studies[35] have shown the structure of the last to be otherwise.

Table 1. Properties of Linkage Isomers

Complex	Infrared Spectrum (cm^{-1})	Visible Spectrum (mμ)	Other Properties	Reference
$[Pd(AsPh_3)_2(NCS)_2]$	Nujol 2089s,b; 854m	351	Non-electrolyte in DMF, stable, yellow	2
$[Pd(AsPh_3)_2(SCN)_2]$	Nujol 2119s,sp; a	395,475sh	Non-electrolyte in DMF, orange	2
$[Pd(bipy)(NCS)_2]$	Nujol 2100s,b; 842m		Non-electrolyte in DMF, yellow, stable	2
$[Pd(bipy)(SCN)_2]$	Nujol 2117m,sp; 700w 2108s,sp		Non-electrolyte in DMF, yellow-orange	2
$[Pd(Et_4dien)NCS]^+$	Nujol 2060,830m		Stable	4
$[Pd(Et_4dien)SCN]^+$	Nujol 2125,710w			4
$[Pd(diphenylphen)(NCS)_2]$	Nujol 2110s,b; a			5
$[Pd(diphenylphen)(SCN)_2]$	Nujol 2120sh; 419 2113s,sp		Stable	5
$[Mn(CO)_5NCS]$	CH_3CN 2113, 813m			6
$[Mn(CO)_5SCN]$	Nujol 2160,676w		Stable, diamagnetic Soluble in organic solvents	6
$[Rh(NH_3)_5NCS]^{+2}$	KBr 2145s,b; 815s	320(ϵ=460) 240sh(ϵ=2200) 215sh(ϵ=5100)	More stable of two	7
$[Rh(NH_3)_5SCN]^{+2}$	KBr 2115s,sp; 730w,b	375 (ϵ=85) 323 (ϵ=220) 280sh (ϵ=450) 233 (ϵ= 1.9 x 10^4)	Quite stable at room temperature	7
$[Ir(NH_3)_5NCS]^{+2}$	KBr 2140s,b; 825s	330sh (ϵ=64) 260sh (ϵ=550) 230sh (ϵ=2000)	More stable of two	7
$[Ir(NH_3)_5SCN]^{+2}$	KBr 2110s,sp; 710 w	355sh (ϵ=35) 310sh (ϵ=100) 275sh (ϵ=180)		7
$[Cr(H_2O)_5NCS]^{+2}$		570 (ϵ=31.4) 410 (ϵ=33.5)	Obtained in solution only	8
$[Cr(H_2O)_5SCN]^{+2}$		620 (ϵ=36) 435 (ϵ=28) 262 (ϵ=1.1 x 10^4)	Obtained in solution only, isomerizes rapidly	8
$[Cu(tripyam)(NCS)_2]$	Nujol 2110s,b 2070sh,b	649,426,380	Brown, stable $\Lambda_M \approx 0$ in DMF	9
$[Cu(tripyam)(NCS)(SCN)]$	Nujol 2128s,sp 2080s,b	700,610,380	Yellow-green, $\Lambda_M \approx 0$ in DMF	9
$[Cu(tripyam)(SCN)_2]$	Nujol 2123s,sp 2100s,sp	720,649,380	Deep-green, $\Lambda_M \approx 0$ in DMF	9

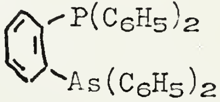
) indicates absorption in given region obscured by organic ligand

s,strong; m,medium; w,weak; b,broad; sp,sharp; sh,shoulder

Related Studies

Closely related to this area of research is the study of selenocyanates which has developed during this decade.[30] By correlating the coordination behavior of the two ligands, many of the hypotheses relating to complexes of thiocyanate can be further investigated and thereby a better understanding attained in regard to the complexities of bonding in coordination compounds in general.

Abbreviations

$AsPh_3$	triphenylarsine
4-cypy	4-cyanopyridine
bipy	2,2'-bipyridine
dien	diethylenetriamine, $NH_2C_2H_4NHC_2H_4NH_2$
diphenylphen	4,7-diphenylphenanthroline
DMF	dimethylformamide
Et_4dien	1,1,7,7-tetraethyldiethylenetriamine, $N(C_2H_5)_2C_2H_4NHC_2H_4N(C_2H_5)_2$
Me_2bipy	4,4'-dimethylbipyridine
4-nitropy	4-nitropyridine
tren	2,2',2''-triaminotriethylamine, $N(CH_2CH_2NH_2)_3$
$\phi_2As\phi P\phi_2$	diphenyl(o-diphenylarsinophenyl)phosphine, 

References

1. A. Turco and C. Pecile, Nature, 191, 66, (1961).
2. F. Basolo, J. L. Burmeister, and A. J. Poë, J. Am. Chem. Soc., 85, 1700 (1963).
3. J. L. Burmeister, Inorg. Seminars, University of Illinois, 1963-1964.
4. F. Basolo, W. E. Baddley, and K. J. Weidenbaum, J. Am. Chem. Soc., 88, 1576 (1966).
5. I. Bertini and A. Sabatini, Inorg. Chem., 5, 1026 (1966).
6. M. F. Farona and A. Wojoicki, ibid., 4, 857 (1965).
7. H. H. Schmidtke, J. Am. Chem. Soc., 87, 2522 (1965).
8. A. Haim and N. Sutin, ibid., 87, 4210 (1965); 88, 434 (1966).
9. G. C. Kulasingam and W. R. McWhinnie, Chem. Ind. (London), 1966, 2200.
10. L. H. Jones, J. Chem. Phys., 25, 1069 (1956).
11. P. C. H. Mitchell and R. J. P. Williams, J. Chem. Soc., 1960, 1912.
12. A. Tramer, J. Chim. Phys., 59, 232 (1962).
13. A. Sabatini and I. Bertini, Inorg. Chem., 4, 1665 (1965).
14. A. Sabatini and I. Bertini, ibid., 4, 959 (1965).
15. J. Lewis, R. S. Nyholm, and P. W. Smith, J. Chem. Soc., 1961, 4590.
16. P. Spacu and D. Camboli, Rev. Roumaine Chim., 11, 157 (1966).
17. (a) Yu. Ya. Kharitonov, G. V. Tsintsadze, and M. A. Porai-Koshits, Russ. J. Inorg. Chem., 10, 427 (1965); (b) Yu. Ya. Kharitonov and G. V. Tsintsadze, ibid., 10, 18, 645 (1965); (c) M. A. Porai-Koshits, ibid., 10, 1537 (1965).
18. S. Fronaeus and R. Larsson, Acta. Chem. Scand., 16, 1447 (1962).
19. R. Larsson and A. Miezis, ibid., 19, 47 (1965).
20. C. Pecile, Inorg. Chem., 5, 210 (1966).

21. C. Schäffer, International Conference on Coordination Chemistry, Chem. Soc. Special Publ., No. 13, 153 (1959).
22. K. A. Taylor, T. V. Long II, and R. A. Plane, J. Chem. Phys., 47, 138 (1967).
23. O. W. Howarth, R. E. Richards, and L. M. Venanzi, J. Chem. Soc., 1964, 3335.
24. S. Ahrland, J. Chatt, and N. R. Davies, Quart. Rev. (London), 12, 265 (1958).
25. R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).
26. C. K. Jørgensen, Inorg. Chem., 3, 1201 (1964).
27. A. Wojcicki and M. F. Farona, J. Inorg. Nucl. Chem., 26, 2289 (1964).
28. A. Wojcicki and M. F. Farona, Inorg. Chem., 3, 151 (1964).
29. J. L. Burmeister and F. Basolo, *ibid.*, 3, 1587 (1964).
30. J. L. Burmeister, Coord. Chem. Rev., 1, 205 (1966).
31. M. F. Farona and A. Wojcicki, Inorg. Chem., 4, 1402 (1965).
32. F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, 3, 1202 (1964).
33. P. Nicpon and D. W. Meek, Inorg. Chem., 6, 145 (1967).
34. K. N. Raymond and F. Basolo, *ibid.*, 5, 1632 (1966).
35. P. C. Jain and E. C. Lingafelter, J. Am. Chem. Soc., 89, 724 (1967).

REACTIONS OF LEWIS BASES WITH BORON HYDRIDES

Peter Welcker October 17, 1967

Introduction

Boron has a low energy p orbital which is empty. In order to fill this orbital and form a chemical bond borane dimerizes to form diborane(6)

$$2BH_3 \longrightarrow B_2H_6$$

or forms Lewis base adducts, such as: $BH_3 \cdot NR_3$

When a Lewis base is allowed to react with diborane(6) these two methods of utilizing the empty orbital are put in competition. The fact that diborane(6) is cleaved by a Lewis base to form two moles of adduct

$$B_2H_6 + 2L \longrightarrow 2LBH_3 \quad ^1$$

indicates that the Lewis base forms a stronger bond with the empty orbital than the hydrogen bridge bonds. All of the boron hydrides are electron deficient. That is, they all have more orbitals than electrons, unlike the one electron per orbital found in most compounds. Due to this electron deficiency all boron hydrides would be expected to react with Lewis bases. The stability of a given reaction will depend on the strength of the Lewis base and the properties of the boron hydride. This seminar will examine the types of reaction taking place between boron hydrides and Lewis bases.

Types of Reactions

The reactions of boron hydrides with Lewis bases may be sorted into three categories: cleavage, displacement, and rearrangement. Cleavage may be either symmetrical or unsymmetrical. Examples of symmetrical cleavage are:

$$B_2H_6 + 2NR_3 \longrightarrow 2BH_3 \cdot NR_3$$

$$B_4H_{10} + 2NR_3 \longrightarrow BH_3 \cdot NR_3 + B_3H_7 \cdot NR_3 \quad ^2$$

Examples of unsymmetrical cleavage are:

$$B_2H_6 + 2NH_3 \longrightarrow BH_2(NH_3)_2^+ + BH_4^- \quad ^3$$

$$B_4H_{10} + 2NH_3 \longrightarrow BH_2(NH_3)_2^+ + B_3H_8^- \quad ^4$$

Ammonia is the best example of an unsymmetrical cleavage.

A study has been made of the cleavage reactions of diborane(6) with trimethylamine, dimethylamine and monomethylamine. [5] Trimethylamine always produces symmetrical cleavage. Dimethylamine produces both symmetrical and unsymmetrical cleavage, but symmetrical cleavage predominates. Methylamine, however, produces far more unsymmetrical cleavage than symmetrical.

Schaeffer, Tebbe, and Phillips [6] propose on the basis of nmr data that the cleavages of tetraborane(10) are initially unsymmetrical and are followed by displacement of a ligand by hydride ion to give a symmetrical result.

Lewis bases may displace either hydrogen or other Lewis base from a boron hydride. An example of hydrogen displacement is the reaction of two moles of Lewis base with one mole of decaborane(14).

$$B_{10}H_{14} + 2L \rightarrow B_{10}H_{12}L_2 + H_2$$

Two mechanisms for the formation of $B_{10}H_{12}L_2$ adduct have been suggested. The first is the case of a ligand which can be protonated,[7] while the second is the case of a non-protonated ligand.[8]

Displacement of ligands by more nucleophilic Lewis bases takes place with the following compounds:

$$BH_2L_2^+, \ ^{9}, \quad BH_3L\ ^{10}, \quad B_9H_{13}L\ ^{11}, \quad B_{10}H_{12}L_2\ ^{12}.$$

The most thoroughly investigated is the last case. The mechanism is apparently a stepwise dissociation and replacement of the less nucleophilic ligand.

There are three prominent examples of rearrangements caused by Lewis bases. The first is:

$$B_{10}H_{16} + 2L \rightarrow B_{10}H_{12}L_2 + 2H_2\ ^{13}$$

Where decaborane(16) has a structure formed by two square pyramidal pentaborane units joined at the apex, and the diligand compound has the decaborane(14) structure.

Icosaborane(16) reacts with two moles of Lewis base to give what was initially thought to be a simple adduct but what the X-ray structure showed to be a rearranged product. [14]

The most thoroughly worked out rearrangement is:

$$B_{10}H_{12}L_2 + 2L' \rightarrow B_{10}H_{10}^{=} + 2HL'^{+} + 2L$$

Hawthorne [15,16] gives the following mechanism which is consistent with the observed kinetics.

$$B_{10}H_{12}L_2 \underset{}{\overset{k_1}{\rightleftarrows}} B_{10}H_{12}L + L$$

$$B_{10}H_{12}L + L' \xrightarrow{k_2} B_{10}H_{11}^{-} + HL'^{+} + L$$

$$B_{10}H_{11}^{-} + L' \xrightarrow{\text{fast}} B_{10}H_{10}^{=} + HL'^{+}$$

$$B_{10}H_{12}L + L' \xrightarrow{k_3} B_{10}H_{12}LL'$$

$$B_{10}H_{12}L \text{ (reactive)} \xrightarrow{k_4} B_{10}H_{12}L \text{ (unreactive)}$$

Decaborane labelled with D in the 1,2,3,4, positions has been converted to $B_{10}H_{10}^{=}$ as has $B_{10}H_{12}$ labelled with a bromine in the 2 position. [17,18] The D are found in equatorial positions as is the bromine.

Recently it has been shown that $B_{10}H_{10}^{=}$ can be opened by the reaction:[19]

$$3(NH_4^+)_2B_{10}H_{10}^{=} + 2HCL + 2Et_2S \rightarrow 2NH_4Cl\cdot(NH_4)_2B_{10}H_{10} + B_{10}H_{12}(Et_2S)_2$$

Trends of Reaction Types

Considering the following series of reactions there is clearly a trend from cleavage and degradation in the smaller boron hydrides to the displacement and rearrangement reactions of the larger molecules.

$$B_2H_6 + 2R_3N \rightarrow 2BH_3R_3N$$

$$B_4H_{10} + \text{ " } \rightarrow BH_3R_3N + B_3H_7R_3N$$

$$B_{10}H_{14} + \text{ " } \rightarrow B_{10}H_{12}(R_3N)_2 + H_2$$

$$B_{10}H_{16} + \text{ " } \rightarrow B_{10}H_{12}(NR_3)_3$$

$$B_{20}H_{16} + 2CH_3CN \rightarrow B_{20}H_{16}(CH_3CN)_2$$

Another example of the increased stability of the larger boron hydrides is the reaction:

$$2R_3N + 6B_2H_6 \rightarrow B_{12}H_{12}^{=} + 2R_3NH^+ + 11H_2 \quad ^{20}$$

The initial reaction must be:

$$2R_3N + B_2H_6 \rightarrow 2R_3N\cdot BH_3$$

and subsequent reactions must combine the adducts and diborane(6) to form the larger boron hydrides. A similar reaction is:

$$B_{10}H_{14} + 2R_3N\cdot BH_3 \rightarrow B_{12}H_{12}^{=} + 2R_3NH^+ + 3H_2 \quad ^{20}$$

If the decaborane(14) is replaced with its diligand compound a variation in products occurs with the variation in ligand strength.

References

1. A. Stock, Hydrides of Boron and Silicon Cornell University Press, Ithaca, N.Y., 1933.
2. R. W. Parry and L. J. Edwards, J. Am. Chem. Soc., 81, 3554 (1959).
3. R. W. Parry, et al., J. Am. Chem. Soc., 80, 4 (1958).
4. G. Kodama and R. W. Parry, J. Am. Chem. Soc., 82, 6250 (1960).
5. S. G. Shore, C. W. Hickam, and D. Cowles, J. Am. Chem. Soc., 87, 2755 (1965).
6. R. Schaeffer, F. Tebbe, and C. Phillips, Inorg. Chem., 3, 1475 (1964).
7. H. C. Beachell and B. F. Dietrich, J. Am. Chem. Soc., 83, 1347 (1961).
8. M. F. Hawthorne, "Boron Hydrides" Chap. 5 in The Chemistry of Boron and its Compounds, E. L. Muetterties (Ed) John Wiley and Sons, New York, N.Y. p. 276.
9. N. E. Miller and E. L. Muetterties, J. Am. Chem. Soc. 86, 1033 (1958).
10. M. F. Hawthorne and W. L. Budde, J. Am. Chem. Soc., 86, 5337 (1964).
11. B. M. Graybill, A. R. Pitochelli and M. F. Hawthorne, Inorg. Chem. 1, 626 (1962).
12. M. F. Hawthorne, R. L. Pilling and R. C. Vasavada, J. Am. Chem. Soc., 89, 1075 (1967).
13. R. N. Grimes, F. E. Wang, R. Lewin and W. N. Lipscomb, Proc. Natl. Acad. Sci. U.S. 47, 996 (1961).
14. J. H. Enemark, L. B. Friedman, and W. N. Lipscomb, Inorg. Chem., 5, 2165 (1966).
15. M. F. Hawthorne, R. L. Pilling and R. N. Grimes, J. Am. Chem. Soc., 86, 5338 (1964).
16. M. F. Hawthorne, R. L. Pilling and R. N. Grimes, J. Am. Chem. Soc., 89, 1067 (1967).
17. A. R. Pitochelli, R. Ettinger, J. A. Dupont and M. F. Hawthorne, J. Am. Chem. Soc., 84, 1057 (1962).
18. T. L. Heying and C. Naar-Colin, Inorg. Chem. 3, 282 (1964).
19. M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams, and J. M. Mathlouf, J. Am. Chem. Soc., 89, p. 3361.
20. H. C. Miller, N. E. Miller and E. L. Muetterties, Inorg. Chem. 3, 1456 (1964).
21. N. N. Greenwood and J. H. Morris, Proc. Chem. Soc., 1963 p. 338.

NEUTRON DIFFRACTION STUDIES OF MAGNETISM IN THE SOLID STATE

David Matthews October 24, 1967

Introduction

In the last ten years neutron diffraction has become one of the primary methods of studying the solid state. The main fields of application are in magnetism and in the location of light atoms. This later use is really an extension of the more conventional X-ray method, but whereas in the X-ray case scattering is proportional to the atomic number of the element, neutron nuclear coherent cross sections vary in a more or less random manner. Scattering from light elements is not swamped by that from heavy elements and in principle all atomic positions in the unit cell can be accurately determined.

The neutron carries a magnetic moment of 1.9 nuclear magnetons and as such interacts with unpaired electron spin density in addition to the nuclear scattering mentioned above. This presentation is mainly concerned with the implication of this interaction for the study of magnetism in the solid state.

Nuclear Scattering Of Thermal Neutrons

Fortunately neutrons in thermal equilibrium with a reactor at around 100°C have wavelengths of just the magnitude needed for the investigation of atomic arrangements. In the case of neutron scattering from nonmagnetic atoms, the neutrons are scattered by the nucleus. The scattering is isotropic due to the fact that the dimensions of the nucleus are small compared to the wavelengths of a thermal neutron (approximately 1Å).

The cross section for nuclear scattering is defined as $\sigma = 4\pi b^2$ where b is the scattering factor for the atom involved. Cassels (1) has shown this to be equal to

$$b = \xi - \frac{\Gamma_n^{(r)}}{2KE_r}$$

ξ = the nuclear radius

$\Gamma_n^{(r)}$ = width of the nuclear resonance for re-emission of the neutron with its original energy

E_r = energy which the neutron must have to produce resonance in the compound nucleus

$K = 2\pi/\lambda$

If the scattering nucleus has spin I, then it may combine with a neutron of spin 1/2 to form a compound nucleus of spin I + 1/2 or I - 1/2. Different scattering lengths b_+ and b_- are associated with these two possibilities. Allowing the further consideration of isotopes, each with a defined abundance and scattering factor, it is possible to define a scattering amplitude for the element. It is this coherent scattering

amplitude b_n which contributes to the Bragg reflection intensities according to:

$$I\alpha|F_{hkl}|^2 = |\sum_n b_n \exp 2\pi i(hx_n + ky_n + lz_n)|^2$$

where the h,k,l are the appropriate Miller indices for the reflection under consideration, the x_n, y_n, z_n are the fractional coordinates of the nth atom in the unit cell, and where the whole exponential expression is derived by considering the phase difference between the contributions from the various nuclei.

Magnetic Scattering

Unpaired electrons give rise to magnetic moments which can interact with the magnetic moment of the neutron and produce neutron scattering in addition to that produced by the nucleus. Paramagnetic substances have completely uncoupled magnetic moments. Halpern and Johnson(2) have shown that a paramagnet with completely quenched orbital angular momentum will have a differential cross section.

$$d\sigma_{PM} = \frac{2}{3} S(S + 1)\left(\frac{e^2\gamma}{mc^2}\right)^2 f^2$$

S = spin quantum number of the scattering atom

γ = magnetic moment of the neutron expressed in nuclear magnetons

f = magnetic form factor

In contrast to nuclear scattering, a form factor occurs in the expressions for magnetic scattering since the electrons determining the magnetic moment have linear dimensions comparable with the neutron wavelength. In certain cases the cross section for magnetic scattering may exceed that for nuclear scattering. However, scattering from a paramagnetic salt is entirely incoherent and will contribute only to the background.

Neutron diffraction intensities can be put on an absolute scale. This implies that f can be accurately determined. The radial distribution of unpaired electron spin can then be found by application of a Fourier transform integral. This is an accurate experimental method of evaluating Hartree-Fock electron distribution calculations.

Measurements of the form factor of Ni^{++} in NiO have been made out to a sin θ/λ value of 0.78 using a wavelength of 1.046 Å (3). This is the first measurement of an aspherical magnetic form factor. The results are interpreted in terms of an aspherical 3d electron distribution. The form factor is written as the sum of a spherical and an aspherical part.

$$f = f_S + f_A$$

The spherical component (f_S) has been correlated with spin polarized Hartree-Fock self consistent field calculations.

In the case of antiferromagnetic and ferromagnetic materials, the magnetic moments of the individual ions are ordered in a defined manner as a result of quantum mechanical exchange forces. According to the

Heisenberg model the interaction is described by a potential energy of the form:

$$U_{ij} = -2J_{ij}S_i \cdot S_j$$

where S_i, S_j are the spin quantum numbers of the two atoms, and J_{ij} is the exchange integral. The existence of defined orientations of the magnetic moments means that there is coherence between neutrons scattered by the individual atoms. In the general case we have a magnetic scattering amplitude defined by:

$$p = \left(\frac{e^2\gamma}{2mc^2}\right)gJf$$

where g is the Lande splitting factor. This scattering amplitude is the magnetic counterpart of the nuclear scattering amplitude b and is associated with the appearance of coherent magnetic peaks dependent in position and intensity on the three dimensional magnetic structure of the lattice.

Detailed consideration of the scattering process (5) shows that when unpolarized neutron beams are used, the total neutron intensity will be proportional to the sum of the absolute values squared of two terms representing nuclear and magnetic scattering. Hence, there is no coherance between the nuclear and magnetic scattering with unpolarized neutrons and the two intensity components are additive.

The most successful method for studying ferromagnetic materials is with the use of polarized neutrons. If the sample is magnetized, neutrons polarized parallel to the magnetic field are scattered such that there is coherence between nuclear and magnetic scattering amplitudes. Observed intensities are much stronger and more accurate magnetic structure determinations are possible.

Magnetic Structure

Among the compounds which have been studied with some prospect of securing a detailed interpretation of the magnetic structure are the perovskites of the transition metals. $CaMnO_3$ was examined by Wollan and Koehler (6) and found to consist of ferromagnetic sheets in the (111) plane with adjacent sheets arranged with opposing moments, giving an antiferromagnetic structure. Anderson's (7, 8) theory of superexchange interactions can be used to rationalize this particular arrangement of magnetic moments.

Ferrous chloride is known to have unusual magnetic properties.(9) The Curie-Weiss constant is positive, which according to Weiss theory corresponds to a positive molecular field and suggests the occurrence of ferromagnetism. Susceptibility measurements at lower temperatures exhibit maxima thereby suggesting antiferromagnetism. Saturation magnetization can be produced by magnetic fields that are much smaller than expected on the basis of a transition temperature of 24°K. A neutron diffraction investigation of $FeCl_2$ has been able to explain these anomalies on the basis of the magnetic structure. (10)

Recently a new type of antiferromagnetic structure has been reported. In order to explain the diffraction pattern of MnO_2, Yoshimori has postulated a helical or screwlike arrangement of spins. (11) A simple

classical model has shown that given suitable interactions such a helical arrangement can minimize the energy. (12)

References

1. J. M. Cassels, Progress in Nuclear Physics: I, ed. O. R. Frisch, Butterworth-Springer, London.
2. O. Halpern and M. H. Johnson, Phys. Rev., 55, 898 (1939).
3. H. A. Alpern, Phys. Rev. Letters, 6, 55 (1961).
4. R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960).
5. G. E. Bacon, Neutron Diffraction, Clarendon Press, Oxford (1955).
6. E. O. Wollan and W. C. Koehler, Phys. Rev., 100, 545 (1955).
7. P. W. Anderson, Phys. Rev., 79, 350 (1950).
8. J. Kanamori, J. Phys. Chem. Solids, 10, 87 (1959).
9. C. Starr, F. Bitter and A. R. Kaufmann, Phys. Rev., 58, 977 (1940).
10. M. K. Wilkinson, E. O. Wollan, J. W. Cable and W. K. Koehler, Phys. Rev., 113, 497 (1959).
11. A. Yoshimori, J. Phys. Soc. Japan, 14, 807 (1959).
12. C. Kittel, Introduction To Solid State Physics, John Wiley and Sons, Inc., New York (1966).

STUDIES OF SOME CYCLOPENTADIENYL COMPOUNDS OF THE REPRESENTATIVE METALS

Joe D. Toney October 31, 1967

Introduction

The cyclopentadienyl compounds of the main group metals have been studied intensively during the past decade. However, widely differing views concerning the structures of these compounds and the nature of the metal ring bonding have been reported. The purpose of this seminar is to review some of the studies which have produced information about the bonding and structures of these M(Cp)(Cp = C_5H_5) compounds.

Mn, Mg, Be

$MnCp_2$, although a transition metal cyclopentadienyl compound, differs widely from other transition metal cyclopentadienyls in that it resembles magnesium dicyclopentadienide in many of its properties. Wilkinson and coworkers[1] have examined some of the physical and chemical properties of $MnCp_2$ and $MgCp_2$, formulating them as ionic cyclopentadienides. $MnCp_2$ shows antiferromagnetic properties and undergoes a change in color of the solid state form at very high temperatures. The infrared spectra and chemical reactions of $MnCp_2$ and $MgCp_2$ imply that ionic bonding exist between the metal and rings of these compounds. Mass spectra data also indicate that the metal-ring bonding in the manganese and magnesium compounds is of a different nature than that in other $M(C_5H_5)_2$ transition metal cyclopentadienyls.[2] Fischer[3] found $MnCp_2$ to be rhombic in the low temperature brown form. $MgCp_2$ [4], on the contrary, was shown to have the same type of monoclinic structure as ferrocene in the solid state. Cotton [5] has shown that $MgCp_2$ retains its sandwich structure in the gaseous state from IR results. He also used molecular orbital theory and ionization potentials to predict that the metal-ring bonding is predominantly of an ionic type. Lippincott and coworkers have examined the infrared spectrum of $MgCp_2$ in detail and made band assignments. [6] They proposed that the metal ring bonding was of a weak covalent type. Turnbull [7] has estimated the Mg-C_5H_5 bond to be 22 Kcal/mole weaker than the Fe-C_5H_5 bond.

Dicyclopentadienyl beryllium was first reported by E. O. Fischer [8] as having a dipole moment of 2.46 D. in benzene and 2.24 D. in cyclohexane. Fischer explained the dipole moment and his infrared spectra by proposing that one cyclopentadienyl ring was σ-bonded and the other ring π-bonded to the beryllium atom. Far infrared spectra obtained by Fritz [9] were not consistent with Fischer's proposal. $BeCp_2$ was shown to have the same type of sandwich configuration in the solid state as $MgCp_2$, $FeCp_2$, etc., on the basis of an X-ray investigation. [10] An electron diffraction study [11] showed that the dipole moment in the beryllium compound resulted from the unsymmetrical position of the metal atom on the C_5 axis between the rings. The molecule is therefore C_5v in the gaseous state. With the above findings in mind, Fritz remeasured the infrared spectra of the solid state and in solution, making assignments of the metal-ring vibrations.[12]

Tl and In

Cyclopentadienyl thallium (I) was first reported by Fischer.[13] The compound was water stable, sublimable, and insoluble in most organic solvents. A half-sandwich structure, which would have a very stable lattice, was proposed for the compound. Cotton has reported the infrared spectrum of the C-H stretching region for gaseous TlCp.[5] Again, Cotton used molecular orbital theory and ionization potentials, to propose an essentially ionic Tl-ring bond. Tyler and coworkers later confirmed a C_5v structure for TlCp from microwave spectra.[14] Indium cyclopentadienyl, which had not been reported when Cotton discussed the TlCp bonding, was later reported by Fischer.[15] Both TlCp and InCp were shown to have chain structures[16] in the solid state with the cyclopentadienyl rings equidistant from the metal atoms. An electron diffraction study of gaseous InCp gave metal-carbon bond lengths which were interpreted as strongly supporting covalent bonding in the molecule.[17]

Sn and Pb

Fischer and coworkers first prepared $SnCp_2$[18] and $PbCp_2$[19] and suggested for them σ-bonded structures on the basis of their dipole moments. Lindstromb[20] noted that the infrared spectra of these compounds closely resembled that of ferrocene. Fritz[21] suggested, from his infrared data, that $SnCp_2$ may contain an ionic metal-ring bond. Wilkinson[22] and coworkers, using infrared, NMR, and U V spectra, proposed an angular sandwich structure for both compounds. The metal atom is therefore, sp^2 hybridized with one orbital containing a lone pair of electrons. One hybrid orbital containing a single electron overlaps with an appropriate ring orbital to form a sigma bond. Fritz later remeasured the infrared spectra of $PbCp_2$ and $SnCp_2$ and found agreement with the proposal of an angular sandwich for them.[23] In the crystalline state[24] $PbCp_2$ has been shown to consist of zigzag chains with bridging cyclopentadienyl rings. However, both $PbCp_2$ and $SnCp_2$ were found to be monomers in the gaseous state.[25]

Groups I-B and II-B

Few reports have been made on the cyclopentadienyl metal complexes of these groups owing to the difficulties encountered in their preparations. Piper and Wilkinson[26] were the first to study $C_5H_5PEt_3Cu$ ($Et = C_2H_5$) and $HgCp_2$ and suggested for them a localized metal-carbon bond on the basis of their U V spectra and chemical properties. The NMR spectra[27] of these compounds show only a single peak at room temperature. Rapid migration of the metal atom between carbon atoms on the ring was suggested to explain these phenomena. Results of a different study on a series of substituted mercury cyclopentadienyls were interpreted as evidence for a sandwich type of structure for $HgCp_2$.[28] Positive proof of the existence of a metal-cyclopentadienyl ring sigma bond was found by Cotton[29] whose NMR data suggested that the metal atom "hopped by a 1,2 scheme on the ring. Whitesides[30] has examined the NMR of $CuPEt_3Cp$ at low temperatures. His data provide evidence for metal-ring sigma bonding. Analysis of the line shapes in the exchange-broadened region indicated that the metal atom migrates by a 1,3 scheme on the cyclopentadienyl ring.

Conclusion

The cyclopentadienyl compounds of the main group metals exhibit many different types of structures. However, the precise nature of the metal ring bonding in a few of these complexes is not completely understood.

References

1. G. Wilkinson, F. A. Cotton, and J. M. Birmingham, J. Inorg. Nucl. Chem., 2, 95 (1956).
2. L. Friedman and G. Wilkinson, J. Am. Chem. Soc., 77, 3689 (1955).
3. E. Weiss and E. O. Fischer, Z. Naturforschg., 10b, 58 (1955).
4. E. O. Fischer and E. Weiss, Z. anorg. u. allgem. chem., 278, 222 (1955).
5. F. A. Cotton and L. T. Reynolds, J. Am. Chem. Soc., 80, 269 (1958).
6. E. Lippincott, J. Xavier, and D. Steele, J. Am. Chem. Soc., 83, 2262 (1961).
7. A. G. Turnbull, J. Inorg. Chem., 6, 805 (1967).
8. E. O. Fischer and H. P. Hoffmann, Chem. Ber., 92, 482 (1959).
9. H. P. Fritz and R. Schneider, Chem. Ber., 93, 1171 (1960).
10. R. Schneider and E. O. Fischer, Naturwissenschaften, 50, 349 (1963).
11. A. Almenningen, et al., J. Chem. Phys., 40, 3434 (1964).
12. H. P. Fritz, J. Organometal. Chem., 5, 501 (1966).
13. E. O. Fischer, Angew. Chem., 69, 207 (1957).
14. Tyler, Cox, and Sheridan, Nature, 183, 1182 (1959).
15. E. O. Fischer and H. P. Hofmann, Angew. Chem., 69, 639 (1957).
16. E. Frasson, F. Menegus, and C. Panattoni, Nature, 199, 1087 (1963).
17. S. Shibata, et. al., J. Chem. Phys., 41, 717 (1964).
18. E. O. Fischer, Z. Naturforsch., 11b, 423 (1956).
19. E. O. Fischer, Z. anorg. Chem., (1956) 286, 237
20. G. Lindstrom, 131st Amer. Chem. Soc. Meeting, Miami, 1957, Abstract 77
21. H. P. Fritz, Chem. Ber., 90, 780 (1959).
22. L. Dave, D. Evans and G. Wilkinson, J. Chem. Soc., 3684 (1959).
23. H. P. Fritz and E. O. Fischer, J. Chem. Soc., 547 (1961).
24. C. Panattoni et. al., Acta. Cryst., (1966) 21, 823.
25. A. Almenningen, et. al., J. Organometal. Chem., 7, (1967) 97.
26. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 2, 32 (1956).
27. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3, 104 (1956).
28. N. S. Kochetkova, Doklady akad. Nauk SSSR 159, 847 (1964).
29. F. A. Cotton, J. Am. Chem. Soc., 88, 4371 (1966).
30. G. M. Whitesides and J. Fleming, J. Am. Chem. Soc., 89, 2855 (1967).

STRUCTURE OF COMPLEX IONS IN MOLTEN SALTS

Charles Kutal November 7, 1967

Introduction

The increasing importance in recent years of high temperature technology has caused renewed interest in the structure and properties of molten salts. Besides their practical aspects, molten salts offer a unique opportunity to test at high temperatures concepts which are useful in aqueous solution. Furthermore, molten salts offer a wide range of solvent types ranging from completely ionic to essentially covalent. We may hope to find a whole new chemistry in these solvent systems which exhibit solubilities, oxidation potentials, and stabilities markedly different from those in water.

The problem of complex formation in molten salts has been an intriguing one for a number of years. Both physicochemical and spectral methods have been used in probing the possible existence of complexes in melts at temperatures up to 1000°C. The results, although not always unambiguous, have shown that even at these extreme temperatures there is a remarkable similarity to species present in aqueous solution.

Physicochemical Methods of Investigation

A. Conductivity

One of the classic means of investigating molten salts is to measure their conductance. Heymann and Mulcahy [1] discussed the relation between the equivalent conductance Λ and the bond types of the alkali and alkaline earth chlorides. Of more interest are the studies [2,3] of the two component systems MX_2-M'X (where M = Cd (II), Ba(II), Pb(II); M' = K^+, Na^+, Li^+; X = Cl^-, Br^-, I^-). Plots of Λ versus composition deviated markedly from linearity and this nonideal behavior was attributed to complex formation. As was later shown, [4] however, this criterion is not always a safe one to use.

B. Cryometry

Cryometric (freezing point depression) techniques have been used with great success in determining the concentration of foreign particles in a solvent. Van Artsdalen [5] studied the freezing point depression of molten $NaNO_3$ caused by added $PbCl_2$, $CuCl_2$, $CdCl_2$, $ZnCl_2$, and $CdBr_2$. In each case the results were consistent with complex formation. The existence of a common ion effect was observed and equilibrium constants for the reactions proposed were calculated.

Spectral Methods of Investigation

A. Electronic Spectra

Gruen and McBeth [6] investigated the spectra of the II, III, IV, and V oxidation states of vanadium in LiCl-KCl eutectic as a function of temperature. They noted changes in the spectra of V(II) and V(III) and attributed this to a change in the coordination number of the ions. The spectra at 400°C were assigned to an octahedrally coordinated species; a transformation to tetrahedral coordination occurred as the temperature was increased. These changes were represented by the equilibria

$$VCl_6^{-4} \rightleftarrows VCl_4^{-2} + 2Cl^- \qquad (1)$$

$$VCl_6^{-3} \rightleftarrows VCl_4^{-} + 2Cl^- \qquad (2)$$

Gruen and McBeth [7] extended their studies in LiCl-KCl eutectic to include the remainder of the first transition series. They noted that Ti^{+3} also underwent an octahedral-tetrahedral transformation of the type described above. The other ions studied showed no spectral changes as a function of temperature, indicating a retention of coordination number.

From a consideration of the free energy of the octahedral-tetrahedral transformation, Gruen and McBeth were able to explain the observed spectral changes. They cited two factors that determined what coordination number an ion would exhibit. The first was electrostatic and favored the formation of the lower charged and thus energetically more favorable MCl_4^- ion over the MCl_6^{3-} ion. The second was the octahedral site stabilization energy which favored formation of a hexacoordinated over a tetracoordinated complex. Of the ions showing no transformation, all except Cr^{+3} exhibited tetracoordination. A strong preference for the formation of the lower charged species in the highly ionic LiCl-KCl melt was thus exhibited.

Gruen and Øye [8] studied the dipositive 3d metal ions in molten aluminum chloride and found that in contrast to LiCl-KCl eutectic, these ions exhibited solely hexacoordination in this covalent melt. They explained this by proposing a solvation model in which the metal dichlorides dissolve in $AlCl_3$ (present as Al_2Cl_6 molecules) according to the equation

$$MCl_2 + 2Al_2Cl_6 = M(Al_2Cl_7)_2 \qquad (3)$$

Since the 3d metal ions form tetracoordinated species in ionic melts and hexacoordinated species in covalent melts, Gruen and Øye [9,10] felt that by using a solvent system that combined the two, valuable information about the octahedral-tetrahedral transformation could be obtained. To this end they chose the system $AlCl_3$-KCl, using Co^{+2} as an indicator of the species formed. Their results are given below:

Mole % KCl	
0-40	Co^{+2} formed a regular octahedral complex. Similar behavior was observed in $GaCl_3$.
42-49	A transformation to a species termed distorted octahedral occurred. Similar behavior was noted in $HgCl_2$.
51	Co^{+2} formed a regular tetrahedral complex. Similar behavior was observed in pyridinium chloride.
100	Co^{+2} formed a distorted tetrahedral complex. Similar behavior was noted in the alkali chlorides: $MgCl_2$, $PbCl_2$, and $CdCl_2$.

Similar studies were made in $ZnCl_2$-$AlCl_3$ melts using Co^{+2} [11] and Ni^{+2} [12] as probes.

B. Raman Spectra

Janz and James [13,14] undertook an investigation of the Raman spectra of solutions of molten $HgCl_2$ containing varying amounts (0-70 mole percent) of added KCl. As the percent Cl^- ion was increased, new spectral lines appeared and intensities varied. The spectra could be explained over the entire composition range if $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{-2}$ were assumed to be the predominant species in the melt. As the concentration of Cl^- ion increases, the high anion affinity and the low shielding efficiency of Hg^{+2} (relative to K^+) favors the formation of $HgCl_3^-$ and $HgCl_4^{-2}$ from the inefficiently shielded $HgCl_2$ or $HgCl^+$.

Conductivity [15] and phase diagram studies [16] are also consistent with the existence of complex ions in $HgCl_2$ melts.

Conclusion

Compared to their gaseous and solid phases, the structure of molten salts has been a somewhat neglected topic. This is no doubt a reflection of the experimental difficulties encountered in studies of this type. Hopefully the physical methods mentioned today can help bridge the gap. One method holding particular promise is the use of transition metal ions (e.g. Co^{+2} or Ni^{+2}) as probes indicating the electrostatic nature of a melt.

References

1. M. F. R. Mulcahy and E. Heymann, J. Phys. Chem., 47, 485 (1943).
2. H. Bloom and E. Heymann, Proc. Roy. Soc. (London), Ser. A., 188, 392 (1947).
3. H. Bloom, I. W. Kraggs, J. J. Molloy, and D. Welch, Trans. Faraday Soc., 49, 1458 (1953).
4. E. R. Van Artsdalen, J. Phys. Chem., 59, 118 (1955).
5. E. R. Van Artsdalen, J. Phys. Chem., 60, 172 (1956).
6. D. M. Gruen and R. L. McBeth, J. Phys. Chem. 66, 57 (1962).
7. D. M. Gruen and R. L. McBeth, Pure Appl. Chem., 6, 23 (1963).
8. H. A. Øye and D. M. Gruen, Inorg. Chem., 3, 836 (1964).
9. D. M. Gruen and H. A. Øye, Paper presented at the 148th meeting of the American Chemical Society, 1964.
10. H. A. Øye and D. M. Gruen, Inorg. Chem., 4, 1173 (1965).
11. C. A. Angell and D. M. Gruen, J. Phys. Chem., 70, 1601 (1966).
12. C. A. Angell and D. M. Gruen, J. Inorg. Nucl. Chem., 29, 2243 (1967).
13. G. J. Janz and D. W. James, J. Chem. Phys., 38, 902 (1963).
14. G. J. Janz and D. W. James, J. Chem. Phys., 38, 905 (1963).
15. G. J. Janz and J. D. E. McIntyre, J. Electrochem. Soc., 109, 842 (1962).
16. I. N. Belyaev and K. E. Mirorov, J. Gen. Chem., (USSR), 22, 1529 (1952).

The following review articles offer a broad background and pertinent references to topics discussed in this seminar.

G. J. Janz, C. Solomons, and H. J. Gardener, Chem. Revs., 58, 461 (1958).
H. Bloom, Revs. Pure Appl. Chem., 9, 139 (1959).
B. R. Sundheim (ed), Ann. N.Y. Acad. Sci., 79, 761-1098 (1960).
J. D. Corbett, Survey Prog. Chem., 2, 91 (1964).

THE KERR EFFECT

Frances Walker November 14, 1967

Introduction:

In this seminar, the Kerr Effect will be discussed from several points of view. I would like to outline the reasons for the observed effect and its implications for molecular structure. Then the work done concerning the dispersion of the Kerr Effect will be discussed. Finally, I will describe some suggestions for useful types of information that can be obtained from the study of this phenomenon in the field of inorganic chemistry.

Electro-Optics:

The Kerr Effect, named for its discoverer John Kerr,[1] concerns the development of double refraction in a normally isotropic medium which is placed in an electric field. That is, when polarized light is passed through this medium it cannot be extinguished by rotation of a prism. This double refraction, or birefringence as it is often called, is due to anisotropy in the refractive index of the material induced by the electric field.

$$D = 2\pi B l E^2 = 2\pi l(n_{\parallel} - n_{\perp})/\lambda$$

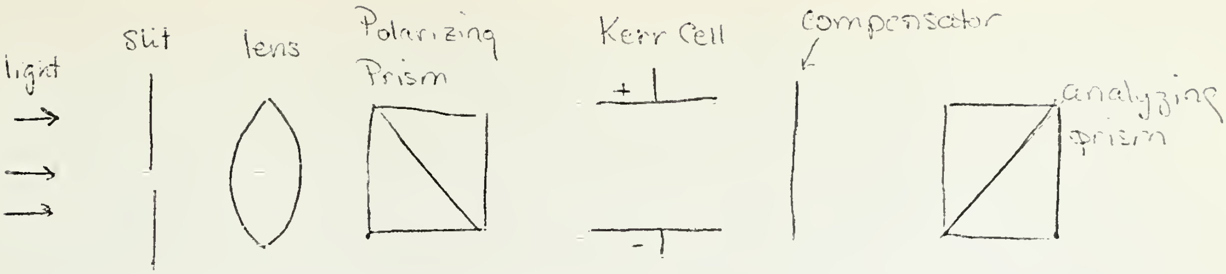
where D = birefringence (in radians), l = cell length (in cm), E = electric field strength, λ = wave length of light used, $n_{\parallel}$ = refractive index of medium parallel to E, $n_{\perp}$ = refractive index of medium perpendicular to E, and B = the Kerr Constant. This expression can be rewritten to give:

$$B = (n_{\parallel} - n_{\perp})/\lambda E^2$$

The difference in $n_{\parallel}$ and n is caused by the field, which induces dipoles of different magnitude and directions parallel and perpendicular to its lines of force.[2,3] The result is that the molecule has anistropic polarizability. All molecules except the completely symmetric (that is, those of tetrahedral, octahedral, or higher symmetry) exhibit anistropy. A compound with a permanent dipole moment has two contributions to B, the most important from the orientation of the dipole with respect to the molecule's principle axis of polarizability and the less important from the induced anistropy. The algebraic sign of B can be either positive or negative, depending on the relative positions of the dipole moment and the axis of maximum polarizability. For a non-polar molecule, B is always positive.

Experimental:

The equipment used to measure the Kerr Effect is fairly uncomplicated in design. Light is passed through a polarizing prism, then through the Kerr Cell, which contains the material to be studied between condensed plates, and finally through some sort of compensating device such as a quarter-wave plate to allow measurement of the amount of double refraction induced. Because light parallel and perpendicular to the field travels at different rates (since $n_{\parallel} \neq n_{\perp}$), the plane polarized light emerges from the cell elliptically polarized (B). A schematic drawing of the Kerr Effect apparatus is shown below:



Applications to Structure Determination:

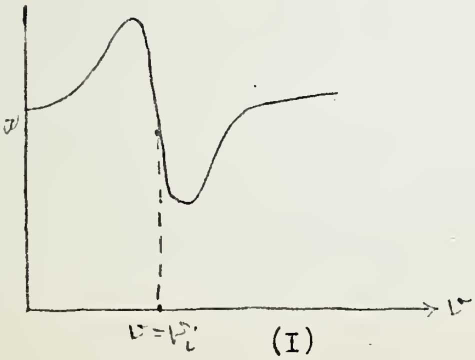
The Kerr Effect has been studied extensively by organic chemists, in particular by Le Fèvre and Le Fèvre [4,5,7,9]. The polarizability of a molecule is described in terms of the three semi-axes of an ellipsoid (b_1,b_2,b_3) which encloses the molecule. To determine these semi-axes, three equations are necessary [10]. One is derived from the Kerr experiment, the second from the electronic polarization, and the third from the depolarization factor. These equations may be found in references 4 and 5. These equations are strictly applicable only to gas phase studies, but workers [4,11] have shown that solutes may be studied in dilute solutions. Kerr Effect studies have provided information on the structures and conformations of organic compounds (e.g., references 12 and 13). Most of these studies involve assuming various possible structures, calculating the expected value of B for each and comparing with the measured value. An example of this type of study is found in references 14 and 6. Determination of the sign of B can also give useful information [2].

Despite the volume of work done on organic compounds, inorganic compounds and complexes have largely been ignored. The Le Fèvres have studied Cu(acac)$_2$ and Be(acac)$_2$ [15] and a series of triphenyl derivatives of Group Va elements.[16]

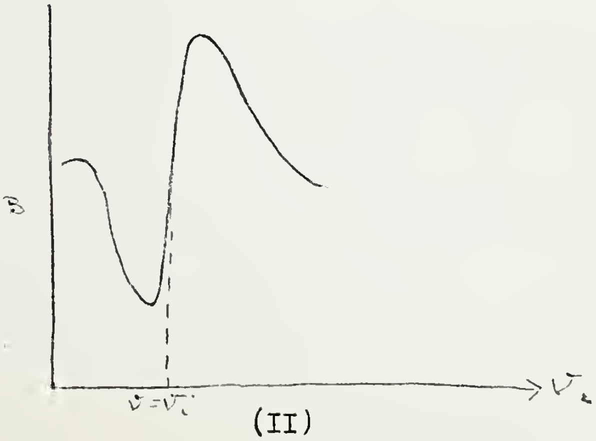
Kerr Dispersion:

A. D. Buckingham has recently proposed [17,18,19] that the behavior of the Kerr Constant in the region of absorption bands of the material being studied should yield useful information. Since B depends directly on the index of refraction, n, dispersion should occur at frequencies corresponding to the absorption frequency ($\nu = \nu_i$). This phenomenon of "anomalous dispersion" is well known for n [20].

Since a transition moment which is polarized parallel to the molecular moment will contribute to $\alpha_{\parallel}$ (the parallel component of the polarizability) but not to $\alpha_{\perp}$, $n_{\parallel} > n_{\perp}$, and the dispersion curve will be like figure (1). For a perpendicular-polarized transition, $n_{\perp} > n_{\parallel}$, and the dispersion curve resembles figure (II).



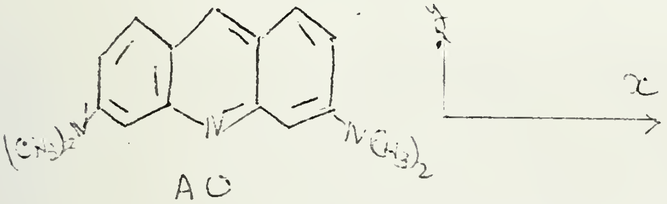
(I)

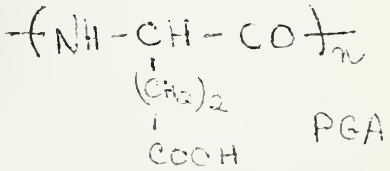


(II)

Other information on the nature of the excited state, such as the magnitude of the transition dipole moment can also be obtained from Kerr dispersion spectra.[19] The electronic Stark Effect gives this same information, but is difficult to measure.[26,27,28] Kerr dispersion has been the subject of several studies, which are discussed below.

The earliest work was done in 1958 by Charney and Halford [21] and was a study of the Kerr dispersion of nitrobenzene in the infrared. They determined the polarization for each of four bands and compared their results with the predictions of group theory. In another study, W. H. Orttung [22] determined that hemoglobin has a dipole moment along its two-fold, or short, exis. Just this year, Powers [23,24] studied an addition compound of acridine orange (AO) and polyglutamic acid (PGA).





He found that a band at 5000 Å due to AO and known to be polarized parallel to AO's x-axis showed positive dispersion. Since PGA has a positive Kerr constant, it must be oriented in the field with its long (polymer) axis parallel to the field. This information indicates that AO must bond to PGA parallel to the polymer axis.

Future Possibilities :

None of these studies have utilized the full possibilities of the Kerr Effect as outlined by Buckingham. [25] There are many areas where the information derivable from these spectra could be used. Assignments of spectra for species such as square planar Platinum complexes could be made, since the polarization of each transition can be determined. Consider for example, $Co(en)_3^{+3}$, for which the energy levels can be determined by group theory by reducing Oh to D_3. However, there is no way to tell whether the E or the A state resulting from the splitting of the T state is higher in energy. A Kerr spectrum should be able to provide this information. Buckingham and Orr [29] have discussed applications of Kerr Effect studies to hyperpolarizability studies.

Other uses of the Kerr Effect are currently being investigated in the field of computer science and laser beam technology, but these topics are beyond the scope of this seminar.

References :

1. J. Kerr, Phil. Mag. 50, 337, 446, (1875).
2. Mansel Davies, Some Electrical and Optical Aspects of Molecular Behavior, Pergamon Press, 1965.
3. C. G. Le Fèvre and R. J. W. Le Fèvre, Rev. Pure Appl. Chem. (Australia), 5, 261 (1955).
4. C. G. Le Fèvre and R. J. W. Le Fèvre, "The Kerr Effect," in Physical Methods of Organic Chemistry, Vol. 1, part III, A. Weissberger, Ed.
5. R. J. W. Le Fèvre, " Molecular Refractivity and Polarizability," in Advances in Physical Organic Chemistry, Vol. III, V. Gold, Ed.
6. J. C. D. Brand and J. C. Speakman, Molecular Structure, Edward Arnold, Ltd., 1960, pp. 177-180.
7. C. G. Le Fèvre and R. J. W. Le Fèvre, J. Chem. Soc., 1953, 4041-50.

8. J. Spencer, Inorganic Seminar, Spring, 1966.
9. R. J. W. Le Fèvre, Australian J. Sci. 18, 3-A, 39-47 (1956).
10. A. D. Buckingham, Chemistry in Britain, 1 (2), 54-9 (1965).
11. C. Y. Chen and R. J. W. Le Fèvre, J. Chem. Soc., 1964, 234.
12. P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fevre, J. Chem. Soc., 1961, 4447-51.
13. J. M. Eckert and R. J. W. Le Fèvre, J. Chem. Soc., 1961, 2356-9.
14. R. J. W. Le Fèvre and C. G. Le Fèvre, J. Chem. Soc., 1935, 1636.
15. R. J. W. Le Fèvre and C. G. Le Fèvre, J. Chem. Soc., 1953, 263.
16. M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, J. Chem. Soc., 1963, 1739-44.
17. A. D. Buckingham, Proc. Phys. Soc. (London), 829, 344(1956).
18. A. D. Buckingham, Proc. Roy. Soc., A, 1962, 267, 271.
19. A. D. Buckingham and D. A. Dows, Discussions Faraday Soc., 1963 (35), 48-57.
20. H. A. Strobel, Instrumental Analysis, Addison-Wesley, pp. 48-53.
21. E. Charney and R. S. Halford, J. Chem. Phys., 29(1) 221-8 (1958).
22. W. H. Orttung, J. Am. Chem. Soc., 87, 924 (1965).
23. J. C. Powers, Jr., J. Am. Chem. Soc., 88, 3679 (1966).
24. J. C. Powers, Jr., J. Am. Chem. Soc., 89, 1780 (1967).
25. L. L. Boyle and C. A. Coulson, Proc. Phys. Soc., 89, 499-502 (1966).
26. J. Lombardi, "The Stark Effect in Electronic Spectra," Physical Chemistry Seminar, Oct. 25, 1967.
27. D. E. Freeman and W. Klemperer, J. Chem. Phys. 45, 52-7 (1966).
28. D. E. Freeman, J. R. Lombardi, and W. Klemperer, ibid, 58-60.
29. A. D. Buckingham and B. J. Orr, Quart. Revs. 21(2), 195-212 (1967).

APPROXIMATE SCF THEORIES

Ronald S. Strange November 21, 1967

Introduction

In recent years the use of the Extended Hückel theory has become quite popular among inorganic chemists for describing the electronic structure of transition metal complexes and other inorganic compounds. This has led to several attempts to improve the results by refining the model. This refinement has taken the direction of trying to simulate the Roothaan-Hartree-Fock Equations; that is, of doing a self-consistent field-like calculation, but retaining the simplicity of the simple theories via careful approximation of difficult integral sums and/or neglect of small valued quantities. These approximate SCF methods shall be the subject of this seminar.

Theory

The solution of the Roothaan-Hartree-Fock Equations involves the solution of the secular equations

$$(\underline{F} - \underline{SE})\, \underline{C} = \underline{0}$$

where

$$(\underline{F})_{ij} = \langle \varphi_i | -1/2\, \Delta^2 - \sum_{A}^{\text{nuclei}} \frac{Z_A}{R_A} | \varphi_j \rangle +$$

$$+ \sum_{k,l} (\underline{R})_{k,l} \left[(ij|kl) - 1/2\, (il)kj) \right],$$

where

$$(\underline{R})_{kl} = 2 \sum_{i}^{\text{occ}} C^*_{ik} C_{il},$$

and

$$\psi_m = \sum_{i=1}^{n} C_{mi}\, \varphi_i$$

$$[(\varphi_i) \text{ are the basis orbitals}],$$

where the $[\psi_m]$ are the molecular orbitals to be determined.[1] Thus the MO's, which are to be determined, appear in the operator via the density matrix $\underline{R}$.

There are N^2 $(\underline{F})_{ij}$'s to be determined, and each involves the sum, $\sum_{k,l}$, which is over N^2 terms. In general, none of these vanish by symmetry, and there is thus a large number of integrals to evaluate, most of which are difficult two, three, and four center two-electron integrals.

Most approximate methods begin by grouping the terms of the matrix elements into appropriate sums over one center terms and sums over many center terms, and then systematically evaluating and/or approximating these.

Pople, et. al.,[2,3,4,5,6]

In the CNDO (complete neglect of differential overlap) method, the zero differential overlap (ZDO) approximation has been applied to the SCF equations in a way that preserves the invariance of the MO's under a coordinate transformation. Thus, the replacement of the carbon 2s, $2p_x$, $2p_y$, $2p_z$ A.O.'s in the basis by the four sp^3 hybrids should yield identical energies in an LCAO-SCF calculation.

The $\{\varphi_i\}$ A.O.'s are treated as an orthonormal set. All two-electron integrals, $(ij|kl)$, are set equal to zero unless $i = j$ and $k = l$. Thus $(ii|jj)$ is non-zero and is designated G_{ij}. Further, all integrals, G_{ij}, are assumed to depend only on the atom to which φ_i and φ_j belong, and each G_{ij} is replaced by G_{AB}. This is severe, but is necessary in order that invariance be preserved under the above approximation.

The core term,

$$H_{ii} = \langle i|-\tfrac{1}{2}\Delta^2 - {}^1/r_A|i\rangle - \sum_{B \neq A} \langle i|{}^1/r_B|i\rangle,$$

is written

$$H_{ii} = \nu_{ii} - \sum_{B \neq A} \langle i|{}^1/r_B|i\rangle.$$

The ν_{ii} are essentially atomic quantities and are evaluated from atomic spectra. For the off-diagonal terms, H_{ij} is neglected for i and j on the same atom, and the nuclear attraction integrals,

$$V_{ij} = \langle i|\frac{Z_B}{r_B}|j\rangle,$$

are set equal to zero unless $i = j$, in which case (for i on Atom A)

$$\langle i|\frac{Z_B}{r_B}|i\rangle = V_{AB}$$

and is the same for all φ_i on atom A. For i and j on different atoms, H_{ij} is written $\beta^{\circ}_{AB}S_{ij}$, where β°_{AB} depends only on the nature of the atom pair.

Due to the neglect of one-center exchange integrals, this method cannot resolve the separation of spin states resulting from the same configuration. This was corrected recently, independently, by Dixon and by Pople, et. al. who added the one-center two-electron integrals.

The exchange modified methods give generally good agreement between calculated and observed bond angles and bond lengths, and gives correctly the qualitative features of the unpaired spin distribution in ethyl and methyl radicals.

Fenske, et. al. [7,8]

Fenske, et. al. first apply the Mulliken approximation to the Fock operator (as Richardson had done) and then separate it into metal and ligand parts:

$$F = -\tfrac{1}{2}\Delta^2 + \sum_{i}^{\text{occ}} \bar{a}_i \underbrace{\{2(X_i X_i| - (X_{j'}|X_{i'}\} - Z_m ({}^1/r_{m'}|}_{\text{metal}} +$$

$$\sum_{j}^{\text{ligands}} \sum_{i}^{\text{occ}} \bar{b}_{ij} \underbrace{\{2(\rho_{ij}\rho_{ij}| - (\rho_{ij'}|\rho_{ij'}\} - Z_j ({}^1/r_j|}_{\text{ligands}}$$

where $\bar{a}_i$ = charge on metal from MO i,

and $\bar{b}_{ij}$ = charge on ligand j from MO i.

The diagonal terms are orbital energies, calculated as a function of population (charge), on the given center plus a term representing the potential of the other atoms, which becomes a crystal field-like term under point charge approximations for the two-electron integrals.

The off-diagonal terms are more complicated, but the core part is formed from appropriate diagonal terms and overlaps, and the potential interaction part is obtained via appropriate point charge approximations.

The principle difficulty of the method lies in the calculation of the many three-center nuclear attraction integrals resulting from the point charge approximation.

The results seem to be quite good for the V, Cr, Fe, and Co hexafluorides, reproducing quite well the experimental $10D_q$ values for these complexes and the experimental B and β values.

Manne [9,10,11]

Manne has used atomic analytical SCF functions as basis orbitals, which simplifies the integral evaluations through atomic Hartree-Fock Eigenvalue relations. Many center two-electron integrals have been approximated by the Mulliken or by the Ruedenberg approximations. The basis orbitals are those for the valence electrons, but are orthogonalized against the core orbitals. Two-center Coulumb integrals are approximated by the Ohno approximation.

This method has calculated the equilibrium bond angle of chlorine trifluoride in good agreement with experiment, and has satisfactorily reproduced the experimental energy shifts due to chemical environment of the $K_{\alpha 12}$ doublet in the X-ray emission spectrum of some sulfur and chlorine oxyanions.

Oleari, et. al. [12,13,14,15,16,17]

Oleari, et. al. have evaluated the one-center parts of the diagonal matrix elements by a very carefully applied use of atomic spectral states and have calculated the many center terms by means of a uniformly charged sphere approximation for the two-center integrals. The off diagonal elements they get from the Wolfsberg-Helmholz formula with K = 1.

In this way they reproduce the ordering of the electronic levels of $[CrO_4]^{=}$ and $[MnO_4]^{-}$ obtained by Ballhausen and Liehr.

Prospect

The outlook seems to point to semiempirical and approximate SCF methods replacing the Extended Hückel method now in use. The more accurate Roothaan calculations over Gaussian basis functions are becoming more and more important. The recent calculations of Csizmadia [18,19] and Clementi [20,21,22,23,24,25] have shown that these calculations are feasible and not too expensive for small molecules and by using "Contracted Gaussian Sets", even medium sized molecules are within reach.

References

1. C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).
2. J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, 5129 (1965).
3. J. A. Pople and G. A. Segal, J. Chem. Phys., 43, 5136 (1965).
4. J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).
5. D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967).
6. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys., 47, 2026, (1967).
7. R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, Inorg. Chem., 5, 951 (1966).
8. R. F. Fenske, K, G. Caulton, D. D. Radtke, and C. C. Sweeney, Inorg. Chem., 5, 960 (1966).
9. R. Manne, Theoret. Chim. Acta. (Berl)., 6, 299 (1966).
10. R. Manne, Theoret. Chim. Acta. (Berl)., 6, 312 (1966).
11. R. Manne, J. Chem. Phys., 46, 4645 (1967).
12. L. Oleari, G. DeMichelis, and L. DiSipio, Mol. Phys. 10, 111 (1966).
13. L. Oleari, L. DiSipio, and G. DeMichelis, Coordin. Chem. Rev., 1, 13 (1966).
14. L. DiSipio, L. Oleari and G. DeMichelis, Coordin. Chem. Rev. 1, 7 (1966).
15. G. DeMichelis, L. Oleari, and L. DiSipio, Coordin. Chem. Rev., 1, 18 (1966).
16. L. Oleari, L. DiSipio, and G. DeMichelis, Coordin. Chem. Rev., 1, 24 (1966).
17. L. Oleari, E. Tondello, L. DiSipio and G. DeMichelis, Coordin. Chem. Rev., 2, 45 (1967).
18. I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, Theoret. Chim. Acta., 6, 191(1966).
19. I. G. Csizmadia, M. C. Harrison, and B. T. Sutcliffe, Theoret. Chim. Acta., 6, 217 (1966).
20. E. Clementi and D. R. Davis, J. Computational Phys., 2, 223 (1967).
21. E. Clementi, J. Chem. Phys., 46, 3842 (1967).
22. E. Clementi, J. Chem. Phys., 46, 3851 (1967).
23. E. Clementi, H. Clementi and D. R. Davis, J. Chem. Phys., 46, 4725 (1967).
24. E. Clementi, J. Chem. Phys., 46, 4731 (1967).
25. E. Clementi, J. Chem. Phys., 46, 4737 (1967).

NUCLEAR MAGNETIC RESONANCE STUDIES OF MOLECULAR MOTION IN SOLIDS

Terence E. Needham December 5, 1967

Introduction

A great deal of information about the motions of molecules or parts of molecules can be obtained by use of broad line nuclear magnetic resonance. One can determine the nature of the motion, its rate, and the activation energy for the motion. In addition one can often calculate one or two structural parameters. The motions examined most often are various kinds of rotational reorientation and molecular diffusion, though occasionally a wobble or more complicated motion shows up.

There are basically two types of nmr experiments which provide information on motion. These are the usual nmr absorption experiment, in which the linewidth and second moment of the absorption curve are the important data, and relaxation time measurements.

Absorption Curve Measurements

Dipole-dipole interactions in the solid state cause the nmr absorption line for a solid to be much broader than that for a liquid. Motion in the solid, however, causes the line to be considerably narrowed compared to the line expected for a rigid lattice. The "second moment" of the absorption curve, $\langle \Delta\omega^2 \rangle$, is defined as $\int_0^\infty (\omega - \langle \omega \rangle)^2 f(\omega)\,d\omega / \int_0^\infty f(\omega)\,d\omega$, where $\omega/2\pi$ is the applied radio frequency, $\langle \omega \rangle$ is $\int_0^\infty \omega f(\omega)\,d\omega / \int_0^\infty f(\omega)\,d\omega$ (ω at the center of the band), and $f(\omega)$ is the function describing the lineshape (1). The second moment is clearly on the order of the square of the linewidth and has the advantage over the linewidth of being more readily calculated theoretically. For identical nuclei (e.g. all protons), the second moment is given (1) theoretically by,

$$\langle \Delta\omega^2 \rangle = \tfrac{3}{2} \gamma^4 \hbar^2 I(I + 1) N^{-1} \sum_{j<k} \frac{(1 - 3\cos^2\theta_{jk})^2}{r^6_{jk}}, \qquad (1)$$

where the sum is over pairs of nuclei, r_{jk} is the internuclear distance, θ_{jk} is the angle between that distance vector and the applied field direction, and N is the number of nuclei considered in the first index, usually all nuclei in a unit cell. The second index then goes over all nuclei. For powder spectra, the $(1 - 3\cos^2\theta_{jk})$ term must be averaged over all lattice orientations. In the case of hindered motions it must also be averaged over all equilibrium positions of the moving species. For continuous motions it must be averaged over the entire motion.

A proposed motion of a species in the solid may then be tested by comparing observed and theoretical second moments, provided that the structure of the solid is known. If, at a particular temperature, the nature of the motion or lack of motion is reasonably certain then a single structural parameter can be incorporated in the r_{jk} and θ_{jk} and calculated from equation (1) and the observed second moment.

The activation energy and reorientation frequency at infinite temperature for a reorientation process can be estimated by plotting the temperature dependence of the linewidths and fitting a theoretical curve to the observed data using the frequency and energy as variable parameters.

Examples

Levy and Grizzle measured linewidths and second moments of a powder sample of $[Me_3SiNSiMe_2]_2$ over the temperature range 77°-300°K, and calculated theoretical second moments for possible motions of the molecule (17). They found that the methyl groups rotate about their C-Si bonds even at 77°K. The observed second moment at this temperature, $8.07 \pm .24G^2$, compared well with the theoretical value of $8.30G^2$ for rotation of the methyl groups. At room temperature, the methyl groups rotate about the C-Si bonds, the Me_3Si groups rotate about the Si-N bonds, and the whole molecule rotates about a molecular axis. A few of the many other second moment studies include $-NH_3$ rotation in ammonia nickel cyanide clathrates (18), rotation of the cyclopentadiene and benzene rings in ferrocene and dibenzenechromium respectively (19), nearly free rotation of perchlorate ions and dioxane molecules in the silver perchlorate-dioxane complex (20), rotation of benzene in the benzene-silver perchlorate complex (21, 22), reorientation of the methyl groups in organosilicon polymërs (23), molecular reorientation or isomerism in bullvalence (24), and rotational reorientation by quantum tunnelling of $-CH_3$ in poly(methyl-α-chlorocrylate) at 1.5°K (25).

Relaxation Measurements

In a solid with molecular motion, the motion of the molecule usually provides the dominant spin-lattice relaxation mechanism except at the lowest temperatures. This process turns out to be most effective when the reorientation frequency is roughly the same as the radiofrequency at which the spin and lattice wish to exchange energy. Thus, the spin-lattice relaxation time, T_1, will reach a minimum at a temperature at which the reorientation process attains that frequency. If the reorientation process can be described by a single reorientation time, τ_c (correlation time), then the relation between τ_c and T_1 is given (3) by,

$$^1/T_1 = C_1\left[\frac{\tau_c}{1+\omega^2\tau_c^{\,2}} + \frac{2\tau_c}{1+4\omega^2\tau_c^{\,2}}\right] , \qquad (2)$$

where $\omega/2\pi$ is the radiofrequency in use and C_1 is a constant. This expression will give a minimum for T_1 where $\omega\tau_c = {}^1/\sqrt{2}$. Far from the minimum equation (2) can be approximated,

for $\omega^2\tau_c^{\,2} \gg 1$,

$$T_1 = 2\omega^2\tau_c/3C_1, \qquad (3)$$

for $\omega^2\tau_c^{\,2} \ll 1$,

$$T_1 = 1/3\tau_c C_1. \qquad (4)$$

For an energy barrier of height E restricting the reorientation, the variation of τ_c with temperature can often be taken as $\tau_c = \tau_\infty \exp(E/RT)$. By plotting log T_1 against $1/T$, one can easily find E from the slope on either side of, and reasonably far from, the minimum.

The spin-spin relaxation time, T_2, for the case of $T_1 \gg T_2$ (often true in solids) is inversely proportional to the linewidth and will give the same information as the linewidth.

Examples

Silvidi, McGrath, and Holcomb (26) measured proton spin-lattice relaxation times for a single crystal of $Ba(ClO_3)_2 \cdot H_2O$ as a function of orientation and temperature. T_1 was measured using the 180°-90° pulse method (10,7). Values ranged from 6 to 2400 seconds. The water molecule does 180° flips about the axis bisecting the H-O-H angle with an activation energy of about 5 kcal/mole. The observed orientation dependence of T_1 is characteristic of intermolecular relaxation between neighboring H_2O molecules rather than of intramolecular relaxation. Sharp dips in T_1 at certain orientations were thought due to cross relaxation with ^{35}Cl.

Anderson (27) studied the temperature dependence of T_1 for 1,3,5-$C_6H_3D_3$ and six solid solutions of C_6H_6 and C_6D_6. The solid solution studies allowed him to sort out the inter- and intra-molecular contributions to T_1 in C_6H_6 since in the limit of low C_6H_6 concentration there can be no intermolecular contribution. The experimental intramolecular T_1 minimum of 196 ± 8 msec at 50 Mc/sec agreed with a calculated value of 199 msec at 50 Mc/sec. Anderson was able to separate out intermolecular and intramolecular contributions to the correlation time τ_c and show that they are equal. This behavior would be expected if the molecular motions were highly correlated, that is if the motion of one molecule strongly influenced the reorientation probabilities of its neighbors.

A few of the other relaxation studies involve molecule rotation and self-diffusion in solids as a function of pressure (28,29), motions in polytetrafluoroethylene (30), diffusion in solid ^3He (31), and methyl rotation in *n*-alkanes (32).

Studies Using Both Techniques

Smith (40), looked at solid triethylenediamine using nmr linewidths, second moments and relaxation times in an attempt to differentiate between the D_{3h} and D_3 molecular configurations. Above 190°K the molecule was found to rotate about the N-N axis with simultaneous wobbling of the axis, with an activation energy of 7 kcal/mole. Above 350°K molecular diffusion becomes important. However, the study was inconclusive with respect to structure determination.

Thompson, Krebs, and Resing (41) examined benzene adsorbed on charcoal and Woessner (42) studied benzene adsorbed on silica gel. In both cases the benzene ring was found to undergo rapid rotation on the surface. Look, Lowe, and Northby (43) carried out T_1, $T_{1\rho}$ ("rotating frame"), second moment, and linewidth measurements on solid H_2S over the range 4.2° to 175°K. They discuss their results in terms of possible structures and motions. Anderson (45) found that, in the hexamethylbenzene-chloranil complex, the hexamethylbenzene molecules rotate rapidly above -109°C whereas nqr measurements indicate that the chloranil molecule may not reorient at all. These, of course, are only a few of many examples.

Selected Bibliography

Theory

1. C. P. Slichter, Principles of Magnetic Resonance. New York: Harper and Row, 1963 (246 pages). A complete detailed mathematical discussion of the whole subject, but is hard to follow.
2. E. R. Andrew, Nuclear Magnetic Resonance. Cambridge, England: Cambridge University Press, 1955, Chapt. 6. An excellent, readable, but not as complete discussion, of solid state nmr.
3. E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London) A216,398-412(1953) Discusses the principle methods with respect to their application to solid cyclohexane.
4. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev., 73(7) 679-705(1948). "Pioneering work" on relaxation.
5. J. H. VanVleck, Phys. Rev., 74(9) 1168-83(1948). Use of second moments.
6. E. R. Andrew, J. Phys. Chem. Solids, 18(1) 9-16(1961) Review of general principles with examples.
7. E. L. Hahn, Phys. Rev., 80(4) 580-594(1950) Spin echoes.
8. W. G. Clark, Rev. Sci. Instr. 35(3), 316 (1964). Pulsed nmr apparatus.
9. T. F. Bolles, Inorg. Seminars, 1962-63, 33-41. Bloch equations.
10. H. Y. Carr and E. M. Purcell, Phys. Rev. 94(3), 630-8 (1954). Diffusion, pulse techniques.
11. H. A. Resing and H. C. Forrey, Phys. Rev. 131(3) 1102-4 (1961). Diffusion.
12. J. E. Anderson and R. Allman, J. Chem. Phys. 47(6) 2178-84 (1967).
13. S. Sykora, Molecular Physics 10(5) 473-7 (1965).
14. E. O. Stejskal and H. S. Gutowsky, J. Chem. Phys. 28(3) 388-96 (1958). Theoretical tunnelling frequency of $-CH_3$ in solids.
15. D. C. Look and I. J. Lowe, J. Chem. Phys., 44(9) 3437 (1966). Good theoretical discussions are also found in references 35-39.

Applications

16. E. R. Andrew and P. S. Allen, J. Chim. Phys. 63(1) 85-91 (1966). This review is essentially a guide to the non-theoretical literature from 1960-65.
17. H. Levy and W. E. Grizzle, J. Chem. Phys., 45(6)1954-60 (1966).
18. K. Umemoto and S. S. Danyluk, J. Phys. Chem. 71(2) 450-2 (1967).
19. L. N. Mulay, E. G. Rochow, and E. O. Fischer, J. Inorg. Nucl. Chem. 4, 231-2 (1957).
20. A. Kawamori, and M. Sakiyama, J. Phys. Soc. Japan, 18, 1218-1219 (1963).
21. D. F. R. Gilson and C. A. McDowell, J. Chem. Phys. 40, 2411 (1964).
22. D. F. R. Gilson and C. A. McDowell, J. Chem. Phys. 39(7) 1825-6 (1963).
23. F. S. Model, G. Redl, and E. G. Rochow, J. Polymer Sci, part A1(4)639-47 (1966).
24. J. D. Graham and E. R. Santee, J. Am. Chem. Soc., 88, 3453-4 (1966).
25. C. D. Knutson and D. M. Spitzer, J. Chem. Phys. 45, 407-8 (1966).
26. A. A. Silvidi, J. W. McGrath and D. F. Holcomb, J. Chem. Phys 41(1)105-11 (1964).
27. J. E. Anderson, J. Chem. Phys. 43(10) 3575-9 (1965).
28. J. E. Anderson and W. P. Shchter, J. Chem. Phys. 44(10) 3647-9 (1965).
29. J. E. Anderson and W. P. Shchter, J. Chem. Phys. 44(5) 1797-1802 (1966).
30. D. W. McCall, D. C. Douglass, and D. R. Falcone, J. Phys. Chem. 71(4) 998-1004 (1967).
31. H. A. Reich, Phys Rev. 129(2) 630-43 (1963).

32. D. C. Douglass and G. P. Jones, J. Chem. Phys. 45(3) 956-63 (1966).
33. D. E. Woessner and B. S. Snowden, J. Phys. Chem. 71(4) 952-5 (1967).
34. D. F. R. Gilson and C. A. McDowell, Nature 183, 1183-4 (1959).
35. G. W. Smith, J. Chem. Phys. 42(12) 4229-43 (1965).
36. Z. M. ElSaffar, J. Chem. Phys., 45(12)4643-7(1966).
37. R. L. Vold and H. S. Gutowsky, J. Chem. Phys. 47(7) 2495-503 (1967).
38. H. S. Gutowsky and G. E. Pake, J. Chem. Phys., 18(2) 162-170 (1950).
39. J. G. Powles and H. S. Gutowsky, J. Chem. Phys. 21(10) 1695-1703 (1953).
40. G. W. Smith, J. Chem. Phys. 43(12)4325-36(1965).
41. J. K. Thompson, J. J. Krebs, and H. A. Resing, J. Chem. Phys., 43(11) 3853-65 (1965).
42. D. E. Woessner, J. Phys. Chem. 70(4) 1217-30 (1966).
43. D. C. Look, I. J. Lowe, and J. A. Northby, J. Chem. Phys. 44(9) 3441-52 (1966).
44. J. H. Loehlin, P. G. Mennitt, and J. S. Waugh, J. Chem. Phys. 44(10) 3912-17 (1966).
45. J. E. Anderson, J. Phys. Chem. 70(3) 927-9 (1966).
46. A. Kawamori, J. Phys. Soc. Japan, 21(6) 1096-1103 (1966).
47. D. S. Schreiber and R. M. Cotts Phys. Rev. 131(3) 1118-32 (1963).

APPLICATIONS OF MAGNETIC CIRCULAR DICHROISM

Gordon Sproul December 7, 1967

Historical Development

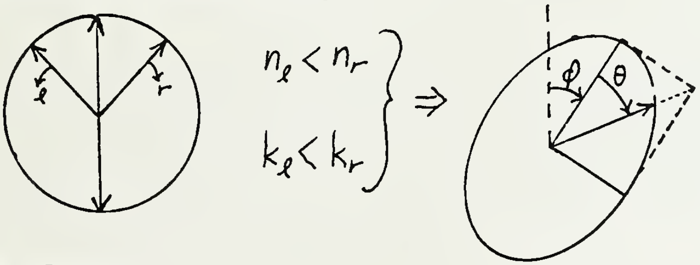
Magnetic circular dichroism (MCD) is the differential absorption of left and right circularly polarized light due to electric and magnetic moments induced in a medium ~~by~~ in a longitudinal magnetic field. It was first reported in 1846 and is commonly referred to as the Faraday effect, after its discoverer. Before the advent of quantum mechanics, there were various treatments of the closely related magnetic optical rotory dispersion (MORD) {or magnetic optical rotation (MOR)}.

$$\varphi = VH_z l$$

where φ is the rotation in degrees, V the Verdet constant (a function of temperature and radiation frequency), the magnetic field, and the sample thickness. From 1929 to 1932 the basic quantum mechanical descriptions to these induced effects were developed; their shortcoming was that they only described the effect far from regions of absorption. It was not until 1964--four years after the through-band treatment of natural optical activity by Moffitt and Moscowitz--that P. J. Stephens presented his Ph.D. thesis.^{2} This thesis has provided the bases for the dozen or so MCD analyses since.

Description

MORD can be visualized as the result of a difference in refractive indexes, n, for left and right polarized light and is measured in degrees φ. MCD is related to the differences in absorption, k, and is measured in degrees θ. If we represent these effects as the superimposed electric vectors of left- and right-circularly polarized light, $n_l < n_r$ will imply that the velocities are $v_l > v_r$ and there will be a phase shift when light passes through a medium of thickness l. Correspondingly (since n is related directly to k) $k_l < k_r$ implies that the left- polarized vector will be decreased in amplitude less than the right-polarized one. These effects can be represented diagrammatically:



Mathematical Development

By relating the observables φ and θ to the refractive indexes and absorption coeffecients, expressing these through Maxwell's equations to the induced moments, and finding the induced moments quantum-mechanically, it is possible to describe the Faraday effect. Assuming a damped oscillator band shape--because it is not possible to know the shape in solution--the following equation results:

$$[\theta(a\to j)]_M = -(24NH/\hbar c)\left(A(a\to j)f_1(\nu,\nu_{ja}) + \{B(a\to j) + [C(a\to j)/kT]\}f_2(\nu,\nu_{ja})\right),$$

where for uniquely oriented or isotropic molecules

$$A(a\to j) = (3/d_a)\sum[\langle j|\mu_z|j\rangle - \langle a|\mu_z|a\rangle]\,\mathrm{Im}\{\langle a|m_x|j\rangle\langle j|m_y|a\rangle\},$$

$$B(a\to j) = (3/d_a)\sum \mathrm{Im}\{\sum_{k\neq a}[\langle k|\mu_z|a\rangle/(W_k-W_a)][\langle a|m_x|j\rangle\langle j|m_y|k\rangle - \langle a|m_y|j\rangle\langle j|m_x|k\rangle]$$
$$+\sum_{k\neq j}[\langle j|\mu_z|k\rangle/(W_k-W_j)][\langle a|m_x|j\rangle\langle k|m_y|a\rangle - \langle a|m_y|j\rangle\langle k|m_x|a\rangle]\},$$

$$C(a\to j) = (3/d_a)\sum\langle a|\mu_z|a\rangle\,\mathrm{Im}\{\langle a|m_x|j\rangle\langle j|m_y|a\rangle\},$$

$$f_1 = \frac{4\nu_{ja}\nu^3(\nu_{ja}^2-\nu^2)\Gamma_{ja}}{h[(\nu_{ja}^2-\nu^2)^2+\nu^2\Gamma_{ja}^2]^2}$$

$$f_2 = \frac{\nu^3\Gamma_{ja}}{(\nu_{ja}^2-\nu^2)^2+\nu^2\Gamma_{ja}^2}$$

where the summation is over all states with the degeneracy in "a" or "j",

where N is Avagadro's number, ν_{ja} is the frequency for the a → j transition, ν is the radiation frequency, Γ_{ja} is the half-width of the a → j transition, d_a is the degeneracy of a, $\vec{m} = e\sum_i r_i$ and $\vec{\mu} = (e/2mc)\sum_i(\vec{l}_i+2\vec{s}_i)$ are electronic and magnetic dipole-moment operators.

The A term is the result of electronic degeneracy of the "a" or "j" states. B arises from mixing of states due to the magnetic field. C is due to a population redistribution due to a Zeeman splitting of the "a" state. It is apparent that B and C are of the same shape, but that the C term is temperature dependent.

Applications

Application of these results has led to assignments of both charge-transfer and d → d transitions. Stephens reported assignments in the charge-transfer spectrum of $K_3Fe(CN)_6$ [8]. Assuming ligand $\gamma_u \to t_{2g}$ transitions, group theory predicts the possible transition state symmetries to be two of the type

$$^2T_{2g} \to {}^2T_{1u}$$

and one of the type

$$^2T_{2g} \to {}^2T_{2u}.$$

The normal absorption spectrum shows three absorption bands at 24,100, 32,900, and 38,460 cm^{-1}. The MCD bands are of the C shape (the B term is assumed negligible) where bands 1 and 3 are negative, while 2 is positive. Using appropriate coupling constants and assuming pure d orbitals for the t_{2g} orbitals, the transition to $^2T_{1u}$ will give a negative,

that to $^2T_{2u}$ a positive number of the correct order of magnitude. These states arise respectively from the ligand t_{1u}^{1} (σ,π) and t_{1u}^{2} (σ,π) and from the ligand t_{2u} (π) orbitals. With only the C term measurable, it is impossible to choose between the two t_{1u} orbitals for the one that produces band 1 or band 3. The A term, which could probably be obtained by increasing the resolution, should give information on the excited state magnetic moments and thus differentiate between these two.

Similar treatments have been carried out for d → d transitions, but here the absorption bands have been generally quite acceptably assigned. However MCD has been shown to be of a significant value in detecting quenching of angular momentum-- the cause being ascribed to the dynamic Jahn-Teller distortion-- and in observing spin-forbidden transitions that are hidden under other d → d (Laporte forbidden) transitions.[4] This latter effect was observed in Cr(III) and is accounted for by two contributing mechanisms:

1. spin forbidden terms can exhibit C terms (normally C⟩⟩A,B) since transition is from a spin degenerate $^4A_{2g}$ ground state, and

2. since transition takes place in the non-bonding quartet-doublet t_{2g}^3 configuration

$$^4A_{2g} \rightarrow {}^2A_{2g}$$

the bands are very sharp and the A term (varying with the reciprocle square of the bandwidth) may be greatly enhanced.

To date neither single crystal nor extensive temperature dependent studies have been reported. With completion of instruments capable of these studies, single crystal analyses will make possible further symmetry restrictions. Low temperature work will quite probably resolve individual vibronic transitions and will enable temperature dependent studies to be made to separate out the B term components.

References
1. W. Moffitt, and A. Moscowitz, J. Chem. Phys., 30, 648 (1959).
2. P. J. Stephens, "Theoretical Studies of Magneto-optical Phenomena," Ph.D. Thesis to University of Oxford, August, 1964.
3. A. D. Buckingham, and P. J. Stephens, Ann. Rvw. Phys. Chem., 17, 399 (1966).
4. A. J. McCaffery, P. J. Stephens, and P. N. Schatz, Inorg. Chem., 6, 1614 (1967).
5. S. F. Mason, Quart. Rvw., 17, 20 (1963).
6. L. Velluz, M. Legrand, M. Grosjenn Optical Circular Dichroism, Academic Press, Inc., N.Y. 1965.
7. C. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Co., Inc. New York, N.Y. 1962, p. 188, p. 235.
8. P. J. Stephens, Inorg. Chem., 4, 1690 (1965).
9. P. N. Schatz, A. J. McCaffery, W. Suëtaka, G. N. Henning, A.B. Ritchie, and P. J. Stephens, J. Chem. Phys. 45, 722 (1966).
10. D. S. Martin, Jr., J. G. Foss, M. E. McCarville, Mary Ann Tucker, and A. J. Kassman, Inorg. Chem., 5, 491 (1966).
11. F. S. Ham, Phys. Rvw., 138, 6A, 1727 (1965).
12. R. G. Denning, J. Chem. Phys. 45, 1307 (1966).
13. M. Born, and E. Wolf, Principles of Optics, MacMillan Co., N.Y., 1964
14. V. E. Shashona, J. Am. Chem. Soc., 86, 2109 (1964).
15. J. G. Foss, and M. E. McCarvilk, J. Am. Chem. Soc., 86, 228 (1964).
16. R. G. Denning, private communication.

ELECTROCHEMISTRY OF ORGANOMETALLIC COMPOUNDS

Howard T. Silverstein December 12, 1967

Introduction

Electrochemical techniques have been used extensively for the investigation of both organic and inorganic systems. Only within the last few years, however, has any work been done on the electrochemistry of organometallic compounds.

The majority of the work on organometallics has involved polarographic analysis of the compounds.[1] In these studies the magnitude of the diffusion current is related to the concentration in solution thru the Ilkovic equation, i.e.,

$$i_d = 607\ nD^{1/2}CK$$

where i_d = diffusion current, D = diffusion coefficient, n = number of faradays of electricity per molar unit of the electrode reaction, K = a constant of the capillary, C = conc. in m. moles/l.

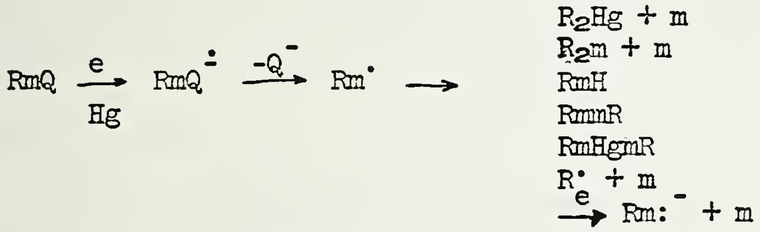
Most of the remaining papers contain little more than the half-wave potentials ($E_{1/2}$) reported as a property of the new compound. Only within the last few years has any attempt been made to correlate this material. This seminar will present a summary and evaluation of the work produced up-to-date.

Instrumentation and Electrochemical Methods

Some good references on instrumentation and methodology can be found in the books by Lingane [2] and Delahay [3] and in the seminar abstract by Albert McDaniel [4].

General Comments

1. The polarographic reduction of the general organometallic RmQ is as follows: [5]



$$RmQ \xrightarrow[Hg]{e} RmQ^{\dot{-}} \xrightarrow{-Q^-} Rm^{\cdot} \longrightarrow \begin{array}{l} R_2Hg + m \\ R_2m + m \\ RmH \\ RmmR \\ RmHgmR \\ R^{\cdot} + m \\ \xrightarrow{e} Rm:^- + m \end{array}$$

where R = organic group, m = metal, Q = another organic group, halogen, or an oxyfunction. The path followed by any specific compound is governed by a variety of factors such as the stability of its radical anion, the interaction of the radical with the electrode, the media or with itself.

2. The polarographic half-wave potential is sensitive to the R group on the metal.[6] When a group -RX is σ bonded to the metal, the half-wave

potential is relatively insensitive to X, however, if R' is π bonded to the metal as in metallocenes, the $E_{1/2}$ is very sensitive to the nature of the substituent.[7]

3. In homologous series of the group IVB and VB elements, the reductions occur at less cathodic potentials as we descend the periodic table.[8,9]

Group lVB Elements

The polarography of tin compounds can be traced to approximately 1950. Costa[10] reported that three waves were observed for the reduction of trialkyl tin halides. Later work casts some doubt on the existence of three separate waves. Dessy using triphenyl tin halides and Allen using trialkyl tin halides both find only two waves.[8] The two waves can be attributed to the following processes:

$$R_3SnCl \xrightarrow{e} \tfrac{1}{2}R_3SnSnR_3 + Cl^- \quad \text{(wave one)}$$

$$\tfrac{1}{2}R_3SnSnR_3 \xrightarrow{e} R_3Sn^- \qquad \text{(wave two)}$$

The same series of reactions occur with dialkyl dihalogen tin compounds.[8] Ph_3SiX and Ph_3GeX undergo a two electron reduction to Ph_3SiH and Ph_3GeH rather than the known $(Ph_3M)_2$ compounds (where M = Ge, Si). Trialkyl lead hydroxide undergoes two one electron reductions. The first leads to R_3Pb-PbR_3 and the second to R_3Pb^-.[11] Triphenyl lead acetate, however, forms Ph_2Hg.[8]

Controlled potential electrolysis of R_3MMR_3 forms R_3M^- anions (M = Sn, Ge, Pb). The reaction of the anions with silver salts appears to form unstable $(R_3MAg)_x$ intermediates.[8]

Group VB Elements

The reduction of group five organometallics leads to a variety of products depending upon the compound type. R_3M compounds all undergo two electron reductions to form R_2M^- compounds. R_2MX compounds undergo a variety of reactions. The P compound forms the diaryl phosphine whereas the As and Sb compounds form the R_2M^- anions. The Bi compound undergoes two sucessive electron reductions to form the unstable R_2Bi^- anion which very rapidly decomposes.

Group IIB Compounds

The most extensively studied element in this group is mercury. The reduction of both aromatic and aliphatic mercury compounds involves two one electron steps.[12,13] The mechanism involves reduction to a free radical and then to the RH compound with deposotion of metallic mercury.[14]

Dessy and coworkers have used the half wave potentials of the second wave as a criteria for determining carbanion stabilities.[15]

The half wave potentials are related to the pKa of the parent RH compounds. They noted a parallel between the half wave potential for the second wave for the reduction of RHgX and the half wave potential for the reduction of R_2Hg compounds.

Rentov and coworkers [16] further investigated the polarography of R_2Hg compounds. They found a better correlation between αE vs. pKa than between E vs. pKa (where α is the charge transfer coefficient.)

Transition Metals

Dessy and coworkers have published a large amount of data on the electrochemistry of transition metal organometallics. The work is still in the preliminary stages of development and the correlations obtained are only tentative. The most important aspect of this work is the presentation of a large body of data that may be useful in further synthetic studies. [5,17]

They have reported the preparation of a large number of stable anions derived from acetylene-metal carbonyl complexes. Controlled potential reduction of these compounds produces a radical anion which has a different reversible oxidation potential than the starting material; yet, all studies show that both compounds are identical. This suggests some sort of reorganizational process taking place relatively slowly after reduction.[18]

The oxidation of biscyclopentadiene compounds has been reported. No clear trend is found for the Fe, Ru, Os triad. [19,20] For the Co, Rh, Ir triad the reductions occur at more negative potentials as we go down the series.

The reduction potentials of substituted ferrocenes have been correlated with Hammett σ values and Taft σ^* values. [21] It has been interpreted in terms of the inductive effect of the substituents. The same has been found for π complexes of Co, Cr, and Ti. [22]

Bimetallic Compounds

The preparation and electrochemistry of a number of bimetallic compounds has been reported.[8,9] In the group IVB and VB homobimetallic compounds, a correlation has been found between the reduction potentials and the strength of the metal to metal bond. As we descend the periodic table, less cathodic potentials are required for reduction.

In the group VIB, VIIB and VIII compounds, the observed trend is that, as we descend the table, more cathodic potentials are required. This leads to the belief that the M-M bond should become stronger as we descend a group. No bond strengths have been reported.

For heterobimetallics three classes have been distinguished. Group A involves compounds where the reduction is somewhere between the reduction potentials for the parent homobimetallics. Type B is where the reduction potential is more anodic than either parent compound. Type C is where the reduction potential is more cathodic than either of the parent compounds. In both types A and B, one electron reductions occur and the fragment that is discharged as an anion corresponds to the fragment whose homobimetallic parent has the most cathodic reduction potential. Case C involves two electrons with the discharge of two anions.

Conclusions

The electrochemistry of organometallic compounds provides information not easily obtainable by other methods. It provides a method of determining the relative energy of metal to metal bonds. This information is of practical use to the synthetic chemist. Combined with a scale of nucleophiliciti it provides a method of synthesis of new metal to metal bonds.

References

1. One good source for references is the biannual reviews of organic polarography in Anal. Chem.
2. J. J. Lingane, " Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N.Y., 1958.
3. P. Delahay, " New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N.Y., 1954.
4. A. McDaniel, University of Illinois Inorganic Seminars, 1967, p. 88.
5. R. E. Dessy, R. B. King and M. Waldrop, J. Am. Chem. Soc., 88, 5112 (1966).
6. M. L. O'Donnall, A. Schwarzhopf and C. W. Kreka, J. Pharm. Sci., 52, 659 (1963).
7. J. Komenda and J. Tirouflet, Compt. rend. 254, 3093 (1962).
8. R. E. Dessy, T. Chivers and W. Kitching, J. Am. Chem. Soc., 88, 453,467 (1966)
9. R. E. Dessy, P. M. Weissman and R. L. Pohl, J. Am. Chem. Soc., 88, 5117 (1966).
10. G. Costa, Gazz. Chim. Ital. 80, 42(1950).
11. I. A. Korshunov and N. I. Malyugina, J. of Gen. Chem. of the U.S.S.R. 31, 982(1961).
12. I. A. Korshunov and N. I. Malyugina, Trudy po Khim i Khim Tekhnol. 4, 296 (1961), in C. A. 55, 26786c (1961).
13. G. Costa, Annali di Chimica Appl. 38, 655 (1949).
14. R. Benesch and R. E. Benesch, J. Am. Chem. Soc., 73, 3391 (1951).
15. R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen and T. Chivers, J. Am. Chem. Soc., 88, 460 (1966).
16. K. P. Butin, I. P. Beletskaya, A. N. Kashin and O. A. Reutov, J. Organometal. Chem. 10, 197 (1967).
17. R. E. Dessy, F. E. Stary, R. B. King and M. Waldrop, J. Am. Chem. Soc., 88, 471, (1966).
18. R. E. Dessy, private communication.
19. J. Page and G. Wilkinson, J. Am. Chem. Soc., 74, 6149 (1952).
20. T. Kuwana, D. E. Bublitz, G. Hoh, J. Am. Chem. Soc. 82, 5811 (1960).
21. G. L. Hoh, W. E. McEwen and J. Kleinberg, J. Am. Chem. Soc., 83, 3948 (1961).
22. H. Hsiung and G. H. Brown, J. Electrochem. Soc. 110, 1085 (1963).

INFRARED INTENSITIES OF THE CO STRETCHING MODES IN METAL CARBONYLS

Donald J. Darensbourg December 14, 1967

Introduction

Infrared spectroscopy has been extensively applied in the study of metal carbonyl compounds. Most of the attention up until recently has been centered on measurements of the CO stretching frequencies. From these measurements force constants are calculated using some simplified force field, usually that of Cotton and Kraihanzel. [1] These calculations are based on the assumption that the π bonding between the metal and the carbon monoxide group determines variations in CO force constants and on a negligible mixing of the CO stretching coordinates with other normal modes of the molecule, e.g. the M-C stretches.

Numerous studies have been made on the sensitivity of the carbonyl stretching frequencies (or force constants) in substituted carbonyl compounds to the nature of the substituent, [2-11] but very few studies have been made on intensity variations. [12-16] This is the matter to which we have directed our attentions.

CO Sigma Bonding Effects

The intensity for the fundamental for CO in the gaseous state is $0.58 \times 10^4 M^{-1} cm^{-2}$, whereas the intensity per CO group in $Mo(CO)_6$ is 12.3×10^4 M^{-1} cm^{-2}, about 21 times larger. It would be of interest to see how the value for free CO would be affected by coordination through σ bond formation at carbon. There are no compounds of sufficient stability available, but data on adsorbed CO have been obtained. [17] These data indicate that the σ contribution to the bond dipole derivative is small compared to the π contribution. The conclusion drawn from this is that to a first approximation infrared intensities of the CO modes in transition metal carbonyls are determined solely by π bonding effects, since in these compounds the π bonding between the metal and the CO group is substantial.[14]

Intensities in $Mo(CO)_5L$ Compounds

The five CO stretches generate reducible representations $\Gamma = 2A_1 + B_1 + E$. Three of these are infrared allowed CO modes, two of symmetry A_1 and one of E symmetry. The coupling of the two A_1 symmetry modes has been examined using both the Cotton-Kraihanzel force field and a more complex force field including Mo-C stretches and interactions. The L matrix elements obtained from the two methods agreed within 2%. It was therefore concluded that the amount of mixing between the two A_1 modes is not sensitive to the assumptions made regarding the nature of the force field. These matrix elements were used to calculate θ, the angle between axial and radial CO groups, assuming equal MCO group dipole moment derivatives for the two A_1 modes. The calculations show that deviation from planarity of the radial CO groups, in addition to coupling, are largely responsible for the observed intensity ratio of the two A_1 symmetry modes.

Dipole moment derivatives were calculated assuming characteristic moments for the A_1 and E modes. It was found that the dipole moment derivative for the E mode was greater than that of the A_1 modes when the ligand substituted for CO was a saturated amine. This is explained by considering interaction effects in the intensities analogous to those giving rise to interaction force constants. The dipole moment derivative for the A_1 mode increases over that of the E mode however, when CO is replaced by a π bonding ligand. This reversal in the ordering of dipole moment derivatives can be accounted for in terms of a transfer of charge from the substituted ligands to CO through the π orbitals during the A_1 stretches.

This constitutes a "vibronic" contribution to the dipole moment derivatives in the A_1 modes.[18] The vibronic contribution from pyridine is very small, however, for the phosphorus and arsenic ligands it is a substantial fraction of the total intensity.

For all P and As ligands in the $Mo(CO)_5L$ series, the dipole moment derivative for the E mode is lower than the value of the derivative for the infrared T_{1u} mode of $Mo(CO)_6$. The type of motion is the same in each case, an anti-symmetric motion of trans CO groups.

The result can be interpreted directly as evidence that there is about the same or less π electron transfer from metal to CO in the $Mo(CO)_5L$ compounds where L is a π bonding ligand, as in the parent carbonyl. This in turn means that there is no increase in π bonding from metal to the remaining CO's when $Mo(CO)_5L$ is formed from the parent carbonyl. This result is clearly at variance with the notion that all decreases in CO frequencies (or force constants) upon substitution can be ascribed to changes in π bonding.[3]

From the decrease in CO force constant upon substitution it can be inferred that there is a net decrease in M-CO σ bond strength, or an increase in M-CO π bonding, or both.[14,19] Intensity data however, shows that there is no increase in the extent of metal-CO π bonding upon substitution for CO by π bonding ligands of P or As. Therefore the decrease in CO force constants are due primarily to weakening of the metal-CO σ bond. This conclusion is fortified by the observation that there is considerable vibronic effect on the A_1 species modes for these ligands, indicating considerable metal-ligand π bonding. Thus the picture is that these ligands have the effect of increasing the electron density on the metal, weakening the metal-carbonyl σ bond. At the same time, the ligand acts as a π acceptor, and lowers the energy of the π orbitals on the metal sufficiently so that there is no net increase in metal-CO π bonding.

Electronic spectral measurements are currently being made in order to substantiate these conclusions based on infrared intensities.

References

1. F. A. Cotton and C. S. Kraihanzel, J. Am. Chem. Soc., 84, 4432 (1962).
2. F. A. Cotton and C. S. Kraihanzel, Inorg. Chem., 2, 533 (1963).
3. F. A. Cotton, Inorg. Chem., 3, 702 (1964).
4. J. B. Wilford and F. G. A. Stone, Inorg. Chem., 4, 389 (1965).
5. A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm and M. H. B. Stiddard, J. Chem. Soc., 3407 (1965).
6. J. Lewis, A. R. Manning and J. R. Miller, J. Chem. Soc., (A), 843 (1966).
7. G. R. Van Heck and W. DeW. Horrocks, Inorg. Chem., 5, 1960 (1966).
8. L. W. Houk and G. R. Dodson, Inorg. Chem., 5, 2119 (1966).
9. W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. G. Graham, Inorg. Chem., 5, 2217 (1966).
10. Herbert D. Kaesz, Robert Bau, David Hendrickson, and J. Michael Smith, J. Am. Chem. Soc., 89, 2844 (1967).

11. R. J. Angelici and Sr. M. D. Malone, Inorg. Chem., 6, 1731 (1967).
12. E. W. Abel and I. S. Butler, Trans. Far. Soc., 63, 45(1967).
13. R. M. Wing and D. C. Crocker, Inorg. Chem., 5, 289 (1967).
14. T. L. Brown and D. J. Darensbourg, Inorg. Chem., 6, 971 (1967).
15. P. S. Bratermann, R. Bau, and H. D. Kaesz, Inorg. Chem., 6, 2097 (1967).
16. D. J. Darensbourg and T. L. Brown, submitted for publication, Inorg. Chem.
17. (a) D. A. Seanor and C. H. Amberg, ibid, 42, 2967 (1965); (b) J. B. Peri, Discussion Faraday Soc., 41, 121 (1966).
18. See T. L. Brown, J. Chem. Phys., 43, 2780 (1965), for a discussion of vibronic contributions to intensities.
19. Gerald R. Dobson, Inorg. Chem., 4, 1673 (1965).

THE POSSIBLE ROLE OF THE TRANSITION METAL IN CERTAIN METALLOCENE SUBSTITUTION REACTIONS

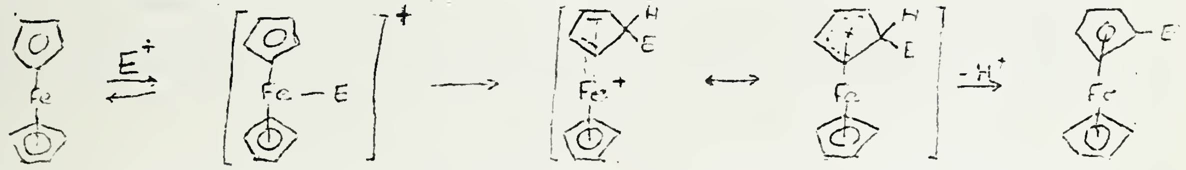
Aaron Burke December 21, 1967

Introduction

Since its discovery in 1951 by Kealy and Pauson,[1] ferrocene has been the object of intensive chemical research. The scope of ferrocene chemistry is so broad it is impossible to review it in anything less than a book. Rosenblum has recently started this.[2] The object of this seminar is to examine one aspect of major importance in ferrocene chemistry: the role of the iron atom in electrophilic substitution reactions and the stabilization of α-ferrocenyl carbonium ions. Earlier investigations concerning these questions have been reviewed by C. E. Coverdale.[3] Recently conflicting models concerning the role of the metal atom have appeared in the literature. The following is a presentation of these models.

Electrophilic Substitution Mechanism

Rosenblum, et al.[4] studied the proton NMR spectrum of ferrocene in strongly acidic media and concluded that direct bonding between the metal atom and proton occurred. Ballhausen and Dahl have suggested that protonation of the metallocenes occur with tilting of the cyclopentadiene rings.[5] Molecular orbital calculations show that variation of ω (the angle defined by the perpendiculars to each ring from the metal atom between 180° and 135° does not cause significant changes in the overlap integral for metal-ring bonds. In addition, this change in geometry would cause a hybridization of the nonbonding metal orbitals resulting in three mutually orthogonal orbitals. The metal atom can then make use of these orbitals in protonation. A recent crystal structure of $(\pi\text{-}C_5H_5)_2MoH_2$ seems to be in agreement with the above model.[6] In 1963, after a kinetic study of the acylation of ferrocene, Rosenblum proposed a general mechanism for electrophilic substitution.[7] This mechanism is pictured below:

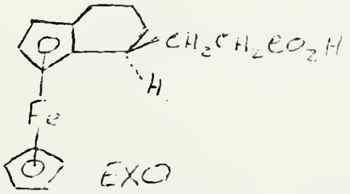


Attack of the electrophile on the metal atom is inferred from the protonation of the metal atom in strongly acidic media. One feature of the mechanism is that substitution must occur preferentially in an endocyclic sense.

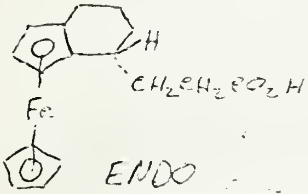
In 1963 Rinehart, Bublitz and Gurtafson [8] studied the acylation of mono, di, and tribridged ferrocenes. They found the reactions to be less stereospecific than in many heteroannularly substituted non bridged alkyl derivatives. The alkyl bridge is assumed to present more steric hinderence for lateral attack in acylation of the positions nearest the bridges. However, the ratio of isomeric products in the various cases do not indicate the high degree of selectivity expected for endocyclic attack. Furthermore, attempts to cyclize the proprionic acid of the tribridged compound with trifluoroacetic acid gave only the trifluoroketone derivative. Friedel-Crafts acylation of the tribridged compound went smoothly. The attacking species in both cases is the positive acylium ion. This suggested that attack in an endocyclic position, which is a necessity in Rosenblum's proposed mechanism does not occur.

Benkesser, Nagai and Hooz [9] while trying to elucidate resonance effects in alkyl substituted ferrocenes made certain observations not in accord with the proposed mechanism. From the rates of desilylation of alkyl substituted ferrocenes, it was noted that resonance effects of the alkyl groups did not fit the order of rate of desilylation. A three step mechanism involving protonation of the metal atom could explain the order. However, a two step mechanism involving exocyclic attack of the proton could rationalize it just as well.

Recently Rosenblum and Abbate synthesized a pair of epimeric proprionic acids shown below:[10,11]



EXO

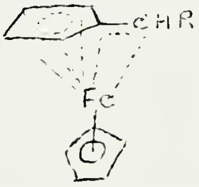


ENDO

The rates of homoannulur cyclization of the exo and endo acids, which by their stereochemistry are constrained to exocyclic and endocyclic attack respectively, might indicate the role of the metal atom in electrophilic substitution of the ring. The exocyclic acid is found to cyclize from four to seven times faster than the endocyclic acid. Rosenblum's conclusion is that the iron atom plays no essential role in the substitution mechanism as he had previously proposed.

α-Carbonium Ion Stabilization

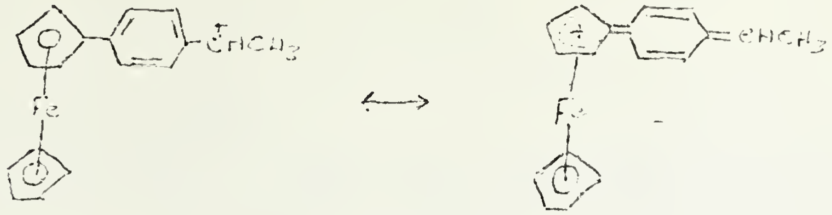
Hill and Richards [12,13,14] after studying the rates of solvolysis reactions of many ferrocenyl carbinyl acetate derivatives proposed a mechanism for these reactions. This mechanism involved direct backside metal participation. The rates of solvolysis were found to be extremely fast and the carbonium ion produced was very stable. A number of the above acetates solvolyz with rates greater than triphenylmethyl acetate. They found the reactions to be completely stereospecific and the rates of solvolysis of the exo form always much greater than the endo rate. These results were said to arise from backside metal participation in the developing carbonium ion. Some crude calculations indicate the possibility of a more stable transition state. Shifting of the ring bearing



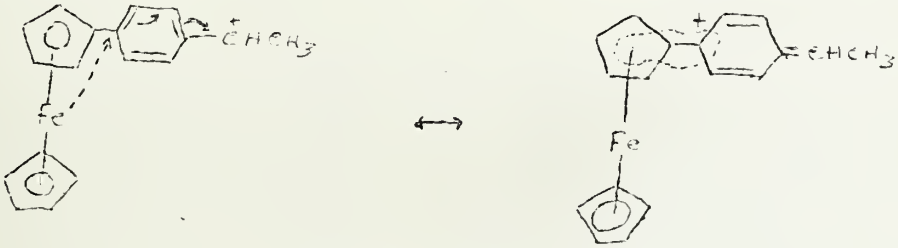
the carbonium ion in the above fashion results in a total increase of the overlap integral. However, the calculations were very crude in nature and the magnitude of the increase was within the range of error for the calculations.

Traylor and his coworkers [15,16,17] have also studied the solvolysis reactions of several ferrocenyl species. They concluded that backside metal participation in these reactions is non-existent. They explain all the experimental data by considering simple σ-π conjugation resonance delocalization of the positive charge onto the ring. They consider the ferrocenyl moiety to be very similar to a methoxy group in resonance stabilizing ability. As a test for their hypothesis they offer data from four experimental techniques (1) effect of resonance stabilizing α groups on α ferrocenyl group acceleration (2) transfer of resonance effects through a phenylene group (3) correlation of SN1 with SN2 reactions on ferrocenylmethyl chloride (4) σ^+ correlations.

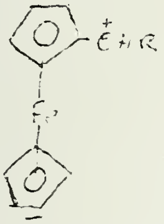
Cais[18] has stated that the resonance structure proposed by Ware and Traylor for the stabilization of the carbonium ion could just as well be explained



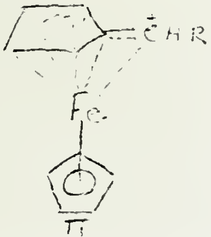
by invoking backside metal participation in resonance forms of the following type:



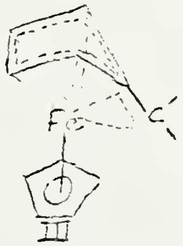
Cais suggests four structures for the carbonium ion which, at the moment, are consistent with the known data. He prefers to interpret the proton NMR spectra of a series of α-ferrocnylcarbinyl cations in terms of Hill and Richards Structure II.



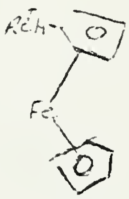
I



II



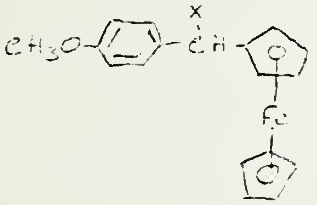
III



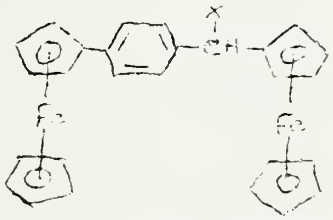
IV

Since it has been possible to isolate salts of the α-ferrocenylcarbonium ions a crystal structure of one might solve the question completely.

Cais is also studying at the present time the solvolysis of the two compounds:



and



Since Ware and Traylor have compared the resonance stabilizing ability of the ferrocenyl moiety to that of the methoxy group ($\sigma_{p\text{-}CH_3O} = .78$ $\sigma_{p\text{-fer}} = 0.71$) a comparison of the rates of solvolysis of the two compounds might substantiate or disprove the analogy.

In conclusion, all that can be said of the moment is that if metal atom participation occurs in the electrophilic substitution mechanism and/or α carbonium ion stabilization, it doesn't occur in as simple minded fashion as inferred from the earlier work.

References

1. J. J. Kealy and P. L. Pauson, Nature, 168, (1951) 1039.
2. M. Rosenblum, " Chemistry of the Iron Group Metallocenes" Part I, John Wiley and Sons, Inc. New York, N.Y., 1965.
3. C. E. Coverdale, Org. Sem. Univ. of Ill., (1962).
4. T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, J. Am. Chem. Soc., 82 (1960) 5249.
5. C. J. Ballhausen and J. P. Dahl, Acta Chem. Scand. 15 (1961) 1333.
6. M. Gerloch and R. Mason, J. Chem. Soc., (1965) 296.
7. M. Rosenblum, J. O. Santer and W. G. Howells, J. Am. Chem. Soc., 85, (1963) 1450.
8. K. L. Rinehart, D. E. Bublitz and D. H. Gustafson, J. Am. Chem.Soc., 85 (1963) 970.
9. R. E. Benkesser, Y. Nagai, and J. Hooz, J. Am. Chem. Soc., 86 (1964) 3742.
10. M. Rosenblum and F. W. Abbate, J. Am. Chem. Soc., 88, (1966) 4178.
11. M. Rosenblum and F. W. Abbate, Adv. Chem. Ser. 62 (1966) 532.
12. J. H. Richards and E. A. Hill, J. Am. Chem. Soc., 81 (1959) 3484.
13. E. A. Hill and J. H. Richards, J. Am. Chem. Soc., 83 (1961) 3840.
14. E. A. Hill and J. H. Richards, J. Am. Chem. Soc., 83 (1961) 4216.
15. J. C. Ware and T. G. Traylor, Tet. Let. 18 (1965) 1295.
16. T. T. Tidwell and T. G. Traylor, J. Am. Chem. Soc., 88 (1966) 3442.
17. T. G. Traylor and J. C. Ware, J. Am. Chem. Soc., 89 (1967), 2304.
18. M. Cais; Organometallic Chem. Rev., 1 (1966) 435.

THE SYNTHESIS, CHARACTERIZATION AND CHEMISTRY OF C-ALKYLAMINE DERIVATIVES OF $B_{10}CH_{13}^-$ and $B_{10}CH_{11}^-$

David Hyatt January 4, 1968

Part 1

The "normal" reaction of a variety of Lewis bases with decaborane-14 has been found to yield a bis-ligand derivative of the $B_{10}H_{14}^{-2}$ class and elimination of one mole of H_2 per mole of $B_{10}H_{14}$. This reaction has been observed with bases such as amines, phosphines, arsines, sulfides, [1] and also for negative ions such as cyanide and hydride. [2]

The reaction of alkyl isonitriles with decaborane, however, has been found to produce, in good yield, a molecule of general formula $B_{10}H_{14}\cdot RNC$ with no hydrogen evolution. Elemental analyses, mass spectral data and osmometric molecular weight data confirm this general formula. The product was further structurally characterized by infrared spectral studies, additional mass spectral studies and boron (^{11}B) and proton nmr investigation.

The infrared spectrum of this molecule, $B_{10}H_{14}\cdot RNC$, showed no absorptions in the $C \equiv N$ region, but did show absorptions which could be attributed to an $R\overset{+}{N}G_2$- function. [3] Exchange studies in D_2O further substantiated this assignment. The presence of the $\overset{H}{B\diagup\;\diagdown B}$ function was also suggested by infrared bands in the region of 1900 cm^{-1}.

In addition to the parent ion peaks in the mass spectrum, there was evidence for the appearance of a fragment of general formula $R_2C{=}\overset{+}{N}R_2$. Similar fragment peaks have been noted in the mass spectra of alkyl amines.

The proton nmr of $B_{10}H_{14}\cdot CNR$ showed normal signals for alkyl protons and showed no N-H coupling. In addition, a broad solvent dependent peak of relative area two was observed. This latter peak was absent in the product obtained from exchange in D_2O; it was assigned to the $-\overset{+}{N}H_2-$ protons. The chemical shift of the methylene protons in the derivative where $R = C_2H_5$ was nearly identical to that reported for other quaternary nitrogen compounds.

The boron(^{11}B) nmr spectrum of $B_{10}H_{14}\cdot RNC$ was complex but could be interpreted as arising from the overlap of 6 doublets; four of relative area (2B) and two of relative area (1B). Such an interpretation suggests a molecule in which the basic framework is that of an icosahedron with one atom removed. The framework contains, then, ten boron atoms and one carbon atom, bearing the alkyl amine function. Two $\overset{H}{B\diagup\;\diagdown B}$ groups may be placed on opposite sides of the open face.

This structure is isostructural with that proposed [4] for $B_9C_2H_{13}$ and reported [5] for $B_{11}H_{13}^{-2}$, both of which are isoelectronic with the $B_{10}CH_{13}^-$ ion. The $B_{10}H_{12}CNH_2R$ molecule may be considered as a zwitterionic derivative of this ion.

The chemistry of $B_{10}H_{12}CNH_2R$ which has been investigated may be conveniently divided into two general areas: (1) Reaction involving the alkyl amine function and (2) Reaction at framework atoms.

The amine protons in $B_{10}H_{12}CNH_2R$ may be removed sequentially by either sodium, sodium hydride, or aqueous base [6] and replaced by methyl groups using either CH_3I or $(CH_3)_2SO_4$. The resultant N-trialkyl derivatives may be treated with sodium or sodium hydride to yield the ionic $B_{10}CH_{13}^-$ species by amine elimination. This latter area of research has been studied by other workers at the University of Illinois as has the preparation of transition metal and non-metal derivatives of the related $B_{10}CH_{11}^{-3}$ ion. [7,8,9]

Halogenation of the $B_{10}H_{12}CNR'_2R$ species has been the most fully studied type of cage substitution investigated and has resulted in the isolation of monobromo, monochloro and dichloro derivatives, proposed to be 4(6) substituted products. The ^{11}B nmr of these derivatives has allowed the tentative identification of the position of substitution.

Attempts to prepare derivatives with substituents at the open face gave only one moderately stable derivative, a carboxylate ester. The structure of this derivative could not be definitely deduced from ^{11}B nmr studies.

The closure of $B_{10}H_{12}CNR'_2R$ to the previously unknown $B_{10}H_{10}CNR'_2R$ was accomplished in nearly quantitative yield by a route involving treatment with NaH and I_2. The "closo" product may be considered as a zwitterionic derivative of the $B_{10}CH_{11}^-$ ion which is isoelectronic with the known $B_9C_2H_{11}$ [10] and $B_{11}H_{11}^{-2}$. [11]

Infrared and ^{11}B nmr data suggest that $B_{10}H_{10}CNR'_2R$ may in fact be isostructural with the known isoelectronic $B_9H_2H_9(CH_3)_2$ [12] and thus can be described as a closo octadecahedral molecule of C_{2v} symmetry.

The stability of the closo molecule was found to be considerably less than that of its nido precursor. Reaction with N-bromo succinimide or NaH gave a nido-monobromo derivative (different than that previously noted) and $B_{10}CH_{13}^-$, respectively.

Part 2

A study of the ^{11}B nmr spectra of $B_{10}H_{12}(\text{ligand})_2$ compounds has been reported in an earlier work [13] and the lowest field doublet in these spectra was assigned to the 2,4 positions. No further elucidation, however, of these spectra was reported and so the following work was undertaken to complete this elucidation.

The previously reported assignment of the 2,4 positions was confirmed by additional 2-Br derivative spectra.

The position of the 5,7,8,10 doublet was assigned by virtue of its integrated area of (4B). The resolution of the 32 Mc spectrometer used was adequate to separate the 5,7,8,10 and 2,4 doublets; such resolution is markedly less complete at 19.3 Mc.

The position of the 1,3 doublet was confirmed as that at highest field by a study of the spectrum of $1,2,3,4\text{-}d_4\text{-}B_{10}H_8[S(C_2H_5)_2]_2$.

The position of the remaining 6,9 doublet was found by a study of the spectra of $B_{10}H_{12}(C_2H_5NC)_2$ and $5,6,7,8,9,10\text{-}d_6\text{-}B_{10}H_6[S(C_2H_5)_2]_2$. The 6,9 doublet was found to shift to higher field in the strong ligand (C_2H_5NC) case and appeared as a shoulder on the upfield side of the 5,7,8,10 peak in the weak ligand $[S(C_2H_5)_2]$ case. A similar study of the spectrum of $B_{10}H_{12}(C_5H_5N)_2$ showed a distinct shoulder on the 5,7,8,10 peak which could be attributed to the 6,9 positions.

The elucidation of the ^{11}B nmr spectra of these compounds (of the $B_{10}H_{14}^{-2}$ class) suggests that, in the absence of complicating factors, the 6,9 doublet shifts to higher field as the strength of the ligand increases. The C_2H_5NC and C_5H_5N ligands are both considered strong ligands, and the former does produce the expected shift. The small shift of the 6,9 positions in the bis-pyridine derivative may arise from secondary back bonding or charge transfer interactions between the ring and cage. [14] Further work at the University of Illinois has shown a similar trend in 6,9 position in cases where negative ions are attached as ligands. [15]

The general observations made in this study, while based on only a limited number of compounds in this class, may, on further study, prove to be generally applicable to compounds of the 2632, $B_{10}H_{14}^{-2}$, type.

References Cited

1. Hawthorne, M. F., Adv. Inorg. Radiochem., 5, 308 (1963).
2. Knoth, W. H., Muetterties, E. L., J. Inorg. and Nucl. Chem., 20, 66 (1961).
3. Heacock, R. A., Marion, L., Can. J. Chem. 34, 1782 (1956).
4. Wiesboeck, R. A., Hawthorne, M. F., J. Amer. Chem. Soc., 86, 1642 (1964).
5. Fritchie, C. J., Jr., Inorg. Chem., 6, 1199 (1967).
6. Knoth, W. H., J. Amer. Chem. Soc., 89, 1274 (1967).
7. Hyatt, D. E., Little, J. L., Moran, J. T., Scholer, F. R., Todd, L. J., J. Amer. Chem. Soc., 89, 3342 (1962).
8. Knoth, W. H., J. Amer. Chem. Soc., 89, 3342 (1967).
9. Little, J. L., Moran, J. T., Todd, L. J., J. Amer. Chem. Soc., 89, 5495 (1967).
10. Tebbe, F., Garrett, P. M., Hawthorne, M. F., J. Amer. Chem. Soc., 86, 4222 (1964).
11. Klanberg, F., Muetterties, E. L., Inorg. Chem., 5, 1955 (1966).
12. Tsai, C., Streib, W. E., J. Amer. Chem. Soc., 88, 4513 (1966).
13. Naar-Colin, C., Heying, T. L., Inorg. Chem., 2, 659 (1963).
14. Graybill, B. M., Hawthorne, M. F., J. Amer. Chem. Soc., 83, 2673 (1961).
15. Hyatt, D. E., Scholer, F. R., Todd, L. J., Inorg. Chem., 6, 630 (1967).

LIBRARY
UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

POLARIZED CRYSTAL SPECTRA OF TRANSITION METAL COMPLEXES

Richard E. DeSimone January 9, 1966

Introduction

Polarized crystal spectra offer many advantages over conventional solution or mull spectra, especially for the study of transition mechanisms, low symmetry fields, and for making reliable assignments of transitions. But compared to the total volume of spectral work reported in the literature, the percent devoted to polarized spectra is relatively small. This is no doubt partly due to the inherent problems associated with this technique, but it is probably also due in large part to a lack of awareness of the advantages which this type of spectrum provides. It is with the hope of rectifying this situation to some meager extent that this topic has been chosen for discussion. We will confine ourselves to the d-d electronic spectra, leaving polarized UV, IR, and Raman spectra as a topic for a future seminar.

Selection Rules

Light is composed of sinusoidally varying electric and magnetic fields which are mutually perpendicular to each other and to the direction of propagation of the wave. [1,2] The interaction of light with matter arises from the perturbing effect of these electric and magnetic fields on the permanent and induced dipole moments of atoms and molecules. From time-dependent perturbation theory we can show that the transition probability for the absorption of radiation is given by [2]

$$A_{m\to n} = \frac{32\pi^3\nu_{mn}^3}{3c^3\hbar}\left\{|(m|e\mathrm{r}|n)|^2 + \left|\left(m\left|\frac{e}{2mc}\mathrm{r}\times\mathrm{p}\right|n\right)\right|^2 + \tfrac{3}{10}\pi^3\frac{\nu_{mn}^2}{c^2}|(m|e\mathrm{rr}|n)|^2\right\}$$

The first term in brackets is the electric dipole term, the second the magnetic dipole term, and the third, the electric quadrupole term. The magnetic dipole and electric quadrupole terms can be shown to be roughly 10^{-5} and 10^{-7} the magnitude of the electric dipole term, from which we can get a rough idea of their significance unless the electric dipole term vanishes.

For the electric dipole mechanism to prevail, the symmetry of the ground state must differ from that of the excited state by the symmetry properties of a translation vector in the molecular point group. [21] The transition probability is given by [11]

$$P_e = \int \Psi_1^* \vec{\mu}_e \Psi_2 \, d\tau$$

where $\vec{\mu}_e = -e\vec{r}$.

If P_e is to be other than zero, the integrand must contain the totally symmetric representation of the point group describing the molecule. Since the d-orbitals are even functions and $\vec{\mu}_e$ is odd, we see immediately that the integral will reduce to zero on symmetry grounds alone. This is the Laporte Rule--all pure electric-dipole d-d transitions are forbidden. [11]

The derivation of the magnetic dipole selection rule is similar. For this type of transition to occur, the symmetries of the ground and excited states must differ by the symmetry properties of a rotation vector in the molecular

point group, and P_m must contain the totally symmetric representation of that group. Analogous to the electric dipole transition probability we have, [11]

$$P_m = \int \Psi_1^* \hat{\mu}_m \Psi_2 \, d\tau$$

$$\mu_{m_x} = -e/2mc \, M_x = -e/2mc \, \frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

Since M_x does not change sign under inversion, the integral for d-orbitals is even and may be non-zero.

Electric quadrupole transitions are rarely, if ever, observed--some have been seen for f-f transitions--and thus will not be further discussed.

One other limitation encountered is that transitions between states of different spin-multiplicity are forbidden because of the orthogonality of the spin wavefunctions which causes all matrix elements between such states to reduce to zero. The mechanism for the breakdown of this rule is spin-orbit coupling. Such spin-forbidden transitions are observed to be very weak.

Polarized Spectra

A polarized crystal spectrum has several advantages over conventional mull or solution spectra. Since in a solution or mull, the particles are randomly oriented, absorption is isotropic and information on mechanism and positive assignments is hard to come by.

In exchange for the considerable bit of extra information a polarized crystal spectrum can provide, certain conditions must be met. First there is the problem of growing crystals large enough and with well-developed faces. These crystals of course must be dichroic. Often, if absorptions are too intense, it is desirable to dope small amounts of metal ion into an isomorphous host lattice. Finally, we must know the orientation of the molecular axis with respect to the external crystal faces. The point to be made here is that while a crystal structure is by no means a requirement, it is nice to have. In other cases, every available means must be used to get the most out of the symmetry properties of the molecule and crystal to determine how the molecule is oriented. While this is not always as difficult as it may seem, it is probably the greatest single drawback to the use of polarized spectra.

For unaxial crystals, polarization experiments provide an extremely simple way of determining the mechanism of a transition. [42,11] This can be illustrated as follows. A spectrum run with light incident along the highest-fold axis of the crystal is called an axial spectrum. A spectrum with light incident to this axis (orthoaxial) may be polarized either perpendicular or parallel, the polarization being determined by the direction of the electric vector. With the electric vector $\perp$ + $\parallel$ the spectra are referred to as σ and π respectively. If the axial and σ spectra coincide, the mechanism is electric dipole, since the electric vectors will coincide in both cases. If the axial and π spectra coincide, the mechanism is magnetic dipole, since the magnetic vectors coincide in both cases.

While a unaxial crystal provides a very convenient method for distinguishing mechanisms, this doesn't preclude the use of biaxial crystals--it just makes the problem more difficult. One must then be completely sure of the molecular orientation if ambiguity in determining selection rules and polarizations is to be avoided. One must also be careful about working with crystals having complicated unit cells, for in such situations the metal ions may often lie along more than one axis and occupy different sites.

Applications

Applications have been generally directed toward studying low symmetry fields, transition mechanisms, and for assigning transitions with the intent of testing the empirical crystal field model. With the rapid development of the crystal-field theory in the 1950's, it was not long before people got around to exploring the obvious advantages of crystal spectra. Yamada *et al.*[45] began a series of studies on the dichroism of several *trans*-$[Co(en)_2X_2]X$ compounds, but did little in the way of investigating transition mechanisms. Ballhausen and Moffitt [32] then took over and gave an interpretation based on the vibronic model [4] of Van Vleck, which did a creditable job of accounting for the observed intensities and polarizations. Using the ionic model for a diamagnetic d^6 complex of D_{4h} symmetry, the polarizations clearly indicated that the 6200 Å band is the $^1A_{1g} \rightarrow {}^1E_g$ transition. Due to a lack of information on the symmetry of the vibrations, the assignment of the upper band was left in doubt and was somewhat arbitrarily assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition.

The work of McClure, [30,31] Holmes, [26] Weakliem, [44] and Ferguson[21-23] on metal ions doped into octahedral and tetrahedral sites in such hosts as Al_2O_3 and ZnO provided much information on the temperature dependence of spectra, noncubic fields, and intensity mechanisms which has been used by virtually all workers in the field since. The technique of doping ions into a host lattice has the advantage of allowing one to pick a particular crystalline environment for study and also to obtain a system about which a great deal of structural information is known.

Some work which is perhaps of more interest to most chemists was done by Piper and Carlin [10,33-36] in their studies of the trisoxalato and tris-acetylacetonato complexes of trivalent first-row transition metals. The studies on the acac's [34] were not quite as fruitful as those on the oxalates, [35] the latter providing a really excellent system for studying trigonal distortions and an environment in which the electronic selection rules are very strictly obeyed. Absorptions were determined to be electric-dipole in nature both for spin allowed and spin forbidden bands. [10]

Further work by Piper and Karipides [38,40] using polarized spectra to study optically active compounds proved quite encouraging and recently Dingle [15] has reported the spectrum of the optically active ion *trans*-$[Co(l\text{-}pn)_2Cl_2]^+$ for which he found the intensities to be about 99% vibronic. He used this to substantiate earlier claims that there is no contribution to the circular dichroism from vibronic coupling.

Hare and Ballhausen [24,25] have studied the polarized crystal spectra of $Ni(NH_3)_4(NCS)_2$ and $Ni(NH_3)_4(NO_2)_2$, and found that the results of their axial field calculations fit the spectrochemical series very nicely. They also studied the tetrakis thiourea nickel chloride system and interpreted their spectra by a centrosymmetric vibronic mechanism.

Ferguson, [23] in a study of transition mechanisms in $KMg(Ni)F_3$ at 20°K has found the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in Ni^{++} is magnetic dipole in origin, one of the few cases where a spin-allowed band has been shown to have magnetic dipole character.

A study of the K_2PtCl_4 crystal was reported by Martin, *et al.*,[28,29] in which a very thorough vibrational analysis was done. On the basis of this and some energy level calculations, it was concluded that several of the excited states probably do not possess the square planar geometry of the ground state.

Recently, an interesting study of the electronic structure of trivalent hexaquo metal ions using polarized spectra was completed by Carlin and Walker.[12,13] These are trigonally distorted systems with monodentate ligands, for which the selection rules allow certain electronic transitions. The ions were doped into a host lattice of guanidine aluminum sulfate hexahydrate(GASH) and various isomorphs which belong to the hexagonal crystal system and grow as well

developed unaxial crystals. On the basis of the sizeable trigonal fields encountered, along with the weak intensities, it was concluded that a vibronic mechanism was operative. Interesting consequences of the low intensities are that it enables identification of the $^4T_{2g}$ band in Cr^{+3} as magnetic dipole in nature, and that it revealed a temperature dependence of the trigonal field--indicated by the variation of band splitting with temperature. This was confirmed by thermal coefficient of expansion measurements.[43]

There are certainly many more examples which could be discussed, some of which are listed in the references.[6-9,14,27,37,39,41] The problems associated with the studies mentioned have by no means conclusively been cleared up and there is certainly ample room for further work in this area. For example; it probably seems by now that everyone believes in the vibronic mechanism as given by VanVleck. However a few years ago, a new theory was proposed by Englman[16-19] which stated that the intensity of d-d transitions arises from mixing of excited states with odd-parity charge-transfer states, via high energy vibrations of the ligands. This theory has been able to accommodate a great many things very nicely, but there is a severe lack of experimental work [20] to test the theory, and much work is certainly needed in this area.

References

1. Kauzmann, W., *Quantum Chemistry*, Academic Press, 1957.
2. Eyring, Walter, and Kimball, Wiley, 1944.
3. Partington, J. R., *An Advanced Treatise on Physical Chemistry*, Vol IV, pp. 101-290, "Physico-Chemical Optics," Longmans-Green and Co., 1953.
4. Cotton, F. A., *Chemical Applications of Group Theory*, Wiley Interscience, 1963.
5. Wood, E. A., *Crystals and Light, An Introduction to Optical Crystallography*, Van Nostrand, 1964.
6. Anex, Ross, and Hedgecock, J. Chem. Phys., 46, 1090 (1967).
7. Belford, R. L., and Carmichael, J. W., J. Chem. Phys., 46, 4515 (1967).
8. " and Piper, T. S., Mol. Phys., 5, 169 (1962).
9. " " " " 5, 251 (1962).
10. Carlin, R. L. Thesis, U. of Illinois, 1960.
11. " " J. Chem. Ed., 40, 135 (1963).
12. Carlin, R. L. and Walker, I. M., J. Chem. Phys., 46, 3921 (1967).
13. " " " " " " 46, 3931 (1967).
14. Carmichael, Steinrauf, and Belford, J. Chem. Phys., 43, 3959 (1965).
15. Dingle, R., J. Chem. Phys., 46, 1 (1967).
16. Englman, R., Mol. Phys., 3, 23, (1960).
17. " " " 3, 48, (1960).
18. " " " 4, 183, (1961).
19. " " " 6, 345, (1963).
20. Fenske, R. F., J. Am. Chem. Soc., 89, 252 (1967).
21. Ferguson, J., Rev. Pure and Appl. Chem., 14, 1, (1964).
22. " , J. Chem. Phys., 35, 1612 (1961).
23. " , " " " 38, 2579 (1963).
24. Hare, C. R., and Ballhausen, C. J., J. Chem. Phys., 40, 788 (1964).
25. " " " " " " 40, 792 (1964).
26. Holmes, O. G., and McClure, D.S., J. Chem. Phys., 26, 1686 (1957).
27. MacFarlane, R. M., J. Chem. Phys., 35, 1240 (1961).
28. Martin, D.S., and Lenhart, C., Inorg. Chem. 3, 1368 (1964).
29. Martin, Tucker, and Kassman, Inorg. Chem., 4, 1682 (1965).
30. McClure, D.S., J. Chem. Phys., 36, 2757 (1962).
31. " " " " 38, 2289 (1963).
32. Moffitt, W., and Ballhausen, C. J., J. Inorg. Nucl. Chem., 3, 178 (1956).

33. Piper, T. S., and Carlin, R. L., J. Chem. Phys., 33, 608, (1960).
34. '' '' '' '' 36, 3330 (1961).
35. '' '' '' '' 35, 1809 (1961).
36. '' '' '' Inorg. Chem., 2, 260 (1963).
37. Piper, T. S., J. Chem. Phys., 35, 1240 (1961).
38. Piper, T. S., and Karipides, A. G., Mol. Phys., 5, 475 (1962).
39. '' '' '' , Inorg. Chem., 1, 970 (1962).
40. '' '' '' , J. Chem. Phys., 40, 674 (1964).
41. Palmer, R. A., and Piper, T.S., Inorg. Chem., 5, 864 (1966).
42. Sayre, E. V., Sancier, K. M., and Freed, S., J. Chem. Phys., 23, 2060 (1955).
43. Walker, I. M., Thesis, Brown Univ., 1967.
44. Weakliem, H., and McClure, D. S., J. Appl. Phys. Suppl., 33, 347 (1962).
45. Yamada, Nakahara, Shimura, and Tsuchida, Bull. Chem. Soc. Japan, 28, 222 (1955).

MECHANISM OF FORMATION OF HYDROGEN CHROMATOPHOSPHATE(2-)[1]

Sven-Åke Frennesson February 6, 1968

I. Introduction: The Stopped-Flow Technique. [2]

The time-scale for the stopped-flow technique extends from that of classical chemical kinetics to half-times of a few milliseconds.

Flow methods rely on especially rapid mixing of the reactants. The principle of flow apparatus was worked out by Hartridge and Roughton [3] in the twenties. The stopped-flow technique was developed primarily by Chance[4] (1940) and Gibson [5] (1952). The flow methods were for a long time mainly used in biochemical work, but during the past decade flow apparatuses [6,7] have been set up in a great number of laboratories, and they have been employed in kinetic studies of a wide variety of chemical reactions in solution. [8]

The apparatus used in this work is based on a design by Sutin and coworkers.[9] It has an eight-jet mixing chamber of teflon. The two reactant solutions are forced into the mixing chamber, where mixing is practically completed within a millisecond. The solution flows from the mixing chamber via an observation tube into a so-called stopping syringe, the piston of which is driven out (by the flowing solution) until it reaches a seating. At that moment the flow of liquid is suddenly stopped, so that the solution comes to rest within about a millisecond.

The observation of the progress of the reaction has to be made with a detection technique that responds rapidly. The most common method involves spectrophotometry. In our apparatus light from a Beckman DU monochromator is sent through the observation tube (internal diameter: 2mm) at a point very close to the mixing chamber and then into a photomultiplier. The changes in absorbance are recorded on a storage oscilloscope, and the trace is photographed with a polaroid camera.

II. Background for the Kinetic Study of $H_2PO_4^- + HCrO_4^- \rightleftharpoons [HO_3P\text{-}O\text{-}CrO_3]^{2-} + H_2O$.

Dinuclear Oxo Complexes, particularly of Cr(VI).

The dichromate ion was one of the first polynuclear ions to be described (1888). The base hydrolysis of dichromate ion was one of the first reactions to be studied by a flow method (1928). [10] A large number of papers have since been published on both the equilibria and the kinetics of the system of dichromate ion and mononuclear chromium(VI) species. [11] The dimerization of vanadate ion and of uranyl ion have also been studied. [12] The rate constants for the formation of the three different dimers are of roughly the same magnitude. Several closely related reactions involving other dinuclear oxo or hydroxo species have been reported recently. [13]

$HCrO_4^-$ is known to undergo condensation not only with itself (to form $Cr_2O_7^{2-}$) but also with many other oxo anions and acids. Spectrophotometric studies show, for instance, that $HCrO_4^-$ reacts with such species as HSO_4^- [14] and $H_2PO_4^-$ [15] to form $[O_3S\text{-}O\text{-}CrO_3]^{2-}$ and $[HO_3P\text{-}O\text{-}CrO_3]^{2-}$, respectively.

Chromato Complexes in Initial Steps of Cr(VI) Oxidations

As early as 1949 Westheimer [16], in a famous review article on chromium(VI) oxidations, postulated the formation of a chromate complex -- an esterification-- as a first step in the oxidation of alcohols. This so-called Westheimer mechanism has also been proposed for Cr(VI) oxidation of aldehydes. [17] Klaning [18] has

found spectrophotometric evidence for 1:1 complexes of $HCrO_4^-$ with acetaldehyde and various alcohols.

Recently such condensations have been suggested as a rapid first step in the Cr(VI) oxidations of As(III) by Mason [19] and of S(IV) as HSO_3^- [20] and $H_2(HPO_3)$ [21] -- both of them by Haight and his research group.

Derivatives of Phosphoric Acid

With this background in mind the Haight and Beattie group, with a strong interest in inorganic mechanisms, wanted to study kinetically such a condensation of $HCrO_4^-$ with another monoacid, without the complication of succeeding redox processes. We decided to study the reaction between $HCrO_4^-$ and $H_2PO_4^-$, thereby also trying to form a link between the field of Cr(VI) reactions and the broad field of reactions involving derivatives of phosphoric acid. This latter group of compounds is very important in biological systems, and the subject of substitution in phosphate esters and other tetrahedral P(V) compounds has been investigated extensively. [22] The hydrolysis of diphosphate ion, $P_2O_7^{4-}$, is very slow.

Equilibrium Measurements

We first studied the equilibrium $HCrO_4^- + H_2PO_4^- \rightleftharpoons [HO_3P\text{-}O\text{-}CrO_3]^{2-} + H_2O$ spectrophotometrically. [14] At 25°C and an ionic strength of 3.0 M, adjusted with $NaClO_4$, the equilibrium constant K_1 was found to be $6 \pm 2\ M^{-1}$. This value is reasonable compared with the value of $3\ M^{-1}$ found by Holloway at ionic strength 0.25 M. [15]

Conditions for the Kinetics Experiments

The optimum pH range is around pH4, where $H_2PO_4^-$ is the principal P(V) species and $HCrO_4^-$ the predominant mono-nuclear Cr(VI) species.

The total Cr(VI) concentration must be low--about 1×10^{-4} M--to keep the concentration of $Cr_2O_7^{2-}$ negligible. [23] On the other hand, the rather low value of the equilibrium constant makes a high phosphate concentration necessary (0.1 to 1 M).

With this large excess of phosphate species the rate of approach to equilibrium follows pseudo-first-order kinetics. We observed the decrease in absorbance at wavelength 350 nm. as the complex was formed. The change in absorbance was only of the order of magnitude of 0.01. Under this condition the recorded trace could be treated as an ordinary concentration-versus-time curve, since absorbance and transmittance are approximately proportional.

The mixing technique of the apparatus caused the two reactant solutions to be mixed in a 1:1 ratio. The ionic strength of both the chromium(VI) solution and the phosphate solution was 3.0 M, adjusted with sodium perchlorate. In a few experiments equilibrium was approached from the opposite direction, i.e., an equilibrium solution containing the complex was diluted with 3.0 M $NaClO_4$ at the moment of mixing.

III. Observed Kinetics and Postulated Mechanism.

Comparison with the Reaction between Cr(VI) and H_2O_2.

The pH-rate profile shows a rapid increase in rate with increasing acidity. At pH < 3.5 the reaction is too fast to be studied by the stopped-flow technique. Around pH4 the observed pseudo-first-order rate constant, k_{obs}, is a linear function of $[H^+]$ at a constant value of the total phosphate concentration, C_P.

At pH > 5, k_{obs} decreases more rapidly with decreasing $[H^+]$ owing to the conversion of $HCrO_4^-$ and $H_2PO_4^-$ into their corresponding bases. The pH dependence suggests the possibility of a mechanism involving a rapid pre-equilibrium, in which H_2CrO_4 (or H_3PO_4) is formed, as has been proposed for the reaction between $HCrO_4^-$ and H_2O_2. [24] This simple mechanism with a rate-determining step between chromic acid and the main phosphate species almost fits our experimental data, when these are presented in a plot of k_{obs} versus $[H^+]$ and another plot of k_{obs} against C_P. But there are small discrepencies.

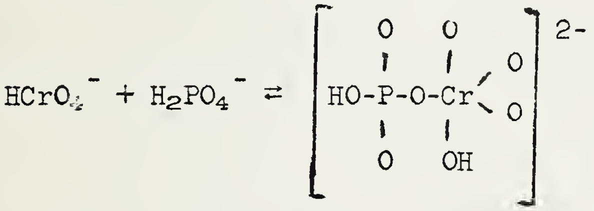
Indication of General Acid Catalysis

The form of the graph, in which k_{obs} is plotted against C_P, suggests that the rate law contains a C_P^2 term, i.e., there is an indication that one of the phosphate molecules acts as a catalyst. Therefore, we made some rate measurements in which acetic acid and sodium acetate had been added to the reactant solutions. A linear dependence of k_{obs} on the total concentration of acetic acid-acetate buffer was observed. The change in slope at varying pH indicates that acetic acid rather than acetate ion is the effective catalyst.

The question of whether Cr(VI) forms a complex with acetic acid is still somewhat controversial. If such a complex is formed, the interpretation of these rate data might be different. To settle this point we plan to do rate measurements with the addition of other acids. We have in fact observed a very small decrease in absorbance when 2M acetic acid is added to a 10^{-4} M Cr(VI) solution. But our kinetic data do not give reason to suspect any interference from an acetate complex. At this stage, therefore, we are inclined to postulate a mechanism that is consistent with general acid catalysis.

Mechanism Involving a Five-coordinated Intermediate.

This led us to postulate a mechanism involving the formation of a 5-coordinated addition intermediate, which loses water in the rate-determining step through the catalytic action of the acidic species present:



$$HCrO_4^- + H_2PO_4^- \rightleftharpoons \left[HO\text{-}\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{P}}\text{-}O\text{-}\overset{\overset{O}{|}}{\underset{\underset{OH}{|}}{Cr}}\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} \right]^{2-}$$

$$[H_2O_3P\text{-}O\text{-}CrO_4H]^{2-} + HB \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} [HO_3P\text{-}O\text{-}CrO_3]^{2-} + HB + H_2O$$

where i = 1,2, and 3 for HB = H_3O^+, H_3PO_4, and $H_2PO_4^-$, respectively. When acetic acid is present, there is an additional path for HB = HAc.

Rate Law

By applying the steady-state approximation to the intermediate or, alternatively, by treating the formation of the intermediate as a rapid pre-equilibrium step--with equilibrium constant K--we obtain a rate expression which at around pH4 has the following form, identical for the forward and reverse reactions:

$$\frac{dx}{dt} = k\ (x_\infty - x)$$

$$k = \left[\frac{k_2K}{K^1_P} C_P^2 + (k_1K + \frac{K_2}{K^1_P}) C_P + k_{-1} \right] [H^+] + k_3KC_P^2 + k_{-3}C_P$$

In these equations x is the concentration of the complex that is formed in the reaction, and K^1_P is the acidity constant for H_3PO_4 (approximately 1.5×10^{-2} M).

At pH > 5, where the principal reactants are losing protons, additional factors are included in the rate law.

Comparison with Observed Kinetics.

By extrapolution to zero phosphate concentration, we obtain $k_{-1} = 2.0 \times 10^{-4}$ $M^{-1}s^{-1}$. This value is similar to the hydrogenation catalyzed path of the hydrolysis of dichromate ion.[25] Since, according to our equilibrium studies, $K_1 = k_1K/k_{-1} = 6M^{-1}$, we get $k_1K = 1.2 \times 10^5$ $M^{-2}s^{-1}$. Similarly, using this relation for the other two pairs of forward and reverse rate constants, we can determine these constants from the slopes and intercepts of the straight lines of the plot of k_{obs} versus $[H^+]$. We evaluated the following constants: $k_{-2} = 600$ $M^{-1}s^{-1}$, $k_2K = 3.5 \times 10^3$ $M^{-2}s^{-1}$, $k_{-3} = 0.9$ $M^{-1}s^{-1}$, and $k_3K = 5$ M^{-2} s^{-1}. The constants thus obtained are in accordance with the rest of the kinetic data.

The forward rate constants cannot be evaluated explicitly, because the equilibrium constant K is unknown. A value of 10^7 to 10^{10} $M^{-1}s^{-1}$ for k_1 is consistent with a reasonable equilibrium concentration for the intermediate (10^{-6} to 10^{-9} M).

Acetic acid produces a slightly bigger effect than $H_2PO_4^-$, which is in accord with the postulate of general acid catalysis.

Exchange with Oxygen-18.

In the mechanistic scheme given above, chromium(VI)--rather than phosphorus(V)--was described as 5-coordinated in the intermediate. It is well-known that the exchange reaction between $HCrO_4^-$ and water is very rapid,[11] while $H_2PO_4^-$ exchanges ^{18}O very slowly with water.[26] Bassam Z. Shakhashiri did a tracer experiment, in which he mixed our reactants ($H_2PO_4^-$ and Cr(VI)) in water labeled with oxygen-18, and then analyzed the phosphate for oxygen-18.[27] No enrichment was found. We conclude that water is lost from chromium(VI), rather than phosphorus(V), in this reaction.

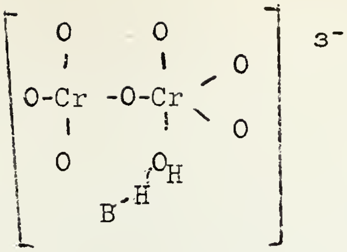
Comparison with the Hydrolysis of Dichromate Ion.

Since the chemical action seems to take place on chromium(VI) in this reaction, the mechanistic picture should have essential similarities with the reaction.

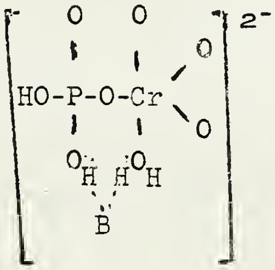
$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2HCrO_4^-$$

In the hydrolysis of $Cr_2O_7^{2-}$ there is H^+ catalysis, but with HAc + Ac^- present only Ac^- is catalytic.[25] Extensive studies on the base hydrolysis of dichromate ion[28] have shown that the basic catalyst is involved in the rate law. The slow step is believed to be a nucleophilic attack on the chromium by the base.[29]

A plausible alternative, however, is that the rate-determining step involves an attack by water in the presence of a base, which transfers a proton from the water to the other chromate center, before the 5-coordinated transitory complex is split. This mechanism, which is similar to ours, involves the following activated complex.



In our case there is also an opportunity for the conjugate base of the catalyst to interact with the extra proton of an OH group on phosphorus:



The detailed mechanism of the rate-determining steps can only be tentative. Since, in our case, the pathway from the 5-coordinated intermediate to the products includes protonation and deprotonation at two different sites in the same ion, it is tempting to assume that each of these steps proceeds according to a concerted mechanism; i.e., a coupling of several elementary steps, as has been proposed for many proton transfer processes, particularly with regard to enzyme catalysis.[30]

Future Plans

We intend to study the influence of acids such as ammonium ion and pyridinium ion on the rate of this reaction.

Our future plans also include further investigation of the kinetics of condensation of different monoacids to form a chromato complex. We next plan to study the formation of hydrogen chromatophosphite(2-), which is not oxidized by chromium(VI).[21]

References

1. J. K. Beattie, S. Frennesson, and G. P. Haight, Jr., to be submitted for publication in J. Amer. Chem. Soc.
2. E. F. Caldin, ''Fast Reactions in Solution,'' Blackwell Scientific Publications, Oxford, 1964, p. 43.
3. H. Hartridge and F. J. W. Roughton, Proc. Roy. Soc., A, 104, 376 (1923).
4. B. Chance, J. Franklin Institute, 229, 455 (1940).
5. G. H. Gibson, J. Physiol., 117, 49P (1952).
6. B. Chance, R. H. Eisenhardt, G. H. Gibson, and K. K. Lonberg-Holm, Ed., "Rapid Mixing and Sampling Techniques in Biochemistry,'' Academic Press, New York, 1964.
7. G. H. Czerlinski, " Chemical Relaxation,'' Dekker, N.Y., 1966 pp. 275-293.
8. H. Strehlow, Annual Rev. Phys. Chem., 16, 167 (1965).
9. G. Dulz and N. Sutin, Inorg. Chem., 2, 917 (1963). The main components of our flow system were supplied by Atom-Mech Machine Co., Patchogue, N.Y.
10. R. N. J. Saal, Rec. Trav. Chim., 47, 73, 275 (1928).
11. R. H. Holyer and H. W. Baldwin, Can. J. Chem., 45, 413 (1967) and earlier references cited therein.

12. M. P. Whittaker, E. M. Eyring, and E. Dibble, J. Phys. Chem., 69, 2319 (1965).
13. N. Sutin, Annual Rev. Phys. Chem., 17, 160 (1966).
14. G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, Inorg. Chem. 3, 1777 (1964).
15. F. Holloway, J. Amer. Chem. Soc., 74, 224 (1952).
16. F. H. Westheimer, Chem. Rev., 45, 419 (1949).
17. R. Stewart, " Oxidation Mechanisms: Applications to Organic Chemistry,'' W. A. Benjamin, Inc., New York, N.Y., 1964 p. 48.
18. U. Klåning, Acta Chem. Scand., 12, 576 (1958).
19. J. G. Mason and A. D. Kowalak, Inorg. Chem., 3, 1248 (1964).
20. G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, J. Amer. Chem. Soc., 87, 3835 (1965).
21. G. P. Haight, Jr., M. Rose, and J. Preer, submitted for publication in J. Amer. Chem. Soc.
22. C. A. Bunton, J. Chem. Educ., 45, 21 (1968), and references therein.
23. Y. Sasaki, Acta Chem. Scand., 16, 719 (1962).
24. M. Orhanović and R. G. Wilkins, J. Amer. Chem. Soc., 89, 278 (1967).
25. B. Perlmutter-Hayman, J. Phys. Chem., 69, 1736 (1965).
26. C. A. Bunton, D. R. Llewellyn, C. A. Vernon and V. A. Welch, J. Chem. Soc., 1636 (1961).
27. B. Z. Shakhashiri and G. Gordon, Talanta, 13, 142 (1966).
28. B. Perlmutter-Hayman and Michael A. Wolff, J. Phys. Chem., 71, 1416 (1967).
29. F. Basolo and R. G. Pearson, " Mechanisms of Inorganic Reactions," 2nd ed., John Wiley and Sons, Inc., 1967, pp. 436-438.
30. M. Eigen, Disc. Faraday Soc., 39, 7 (1965).

PHOSPHORUS (31) NMR

W. D. Perry February 22, 1968

Introduction[1,2]

The purposes of this seminar are to present the basic principles that are necessary to the use of P^{31} nuclear magnetic resonance, and to demonstrate the kinds of information which are of interest to the inorganic chemist that can be obtained.

The only stable isotope of phosphorus, P^{31}, has a non-zero spin, $I = 1/2$, and a magnetic moment of $\mu = 1.1305$ nuclear magnetons. Due to this smaller magnetic moment as compared to that of hydrogen, the sensitivity of phosphorus to the nuclear magnetic resonance experiment is only 6.64 percent that of an equal number of hydrogen nuclei.

Despite this lack of sensitivity, the P^{31} nucleus is well suited for study by high resolution nuclear magnetic resonance techniques. It gives rise to sharp signals with rather large chemical shifts. The range of P^{31} chemical shifts is about 600 ppm, and the shifts are generally measured with respect to an external sample of 85% orthophosphoric acid, H_3PO_4.

In considering the P^{31} resonance shifts, two factors not present in the case of hydrogen or fluorine are encountered. First, phosphorus is multivalent, and second, it has two stable valence states (+3, +5). The minimum concentration of P^{31} nuclei which can be detected at 14,096 gauss and 24.3 mc/sec is approximately 0.02 M.

Recent review articles [1,13,21] on P^{31} nuclear magnetic resonance list over 3,000 phosphorus compounds that have been studied by this method.

Theory[3-13,22]

Shifts of the P^{31} resonance signal with differing chemical environment was first reported by Knight [3] in 1949 and later by Dickenson. [4]

It has been shown by Ramsey [5,6] that the shielding coefficient for heavy nuclei is dominated by the second order paramagnetic term. This is in contrast to hydrogen for which the diamagnetic term is the dominating factor in the determination of the chemical shift. Thus, the theoretical interpretation of P^{31} chemical shift data presents a much more difficult problem than does the familiar case of hydrogen.

Muller, et al., [7] have examined a series of phosphorus containing compounds and have subjected their results to a semi-empirical analysis in an attempt to correlate P^{31} chemical shifts with bond properties such as hybridization, degree of ionicity, and double bond character. Following a procedure similar to that of Saika and Slichter [8] for F^{19}, they assumed that the second order paramagnetic term makes the dominant contribution to the shielding of the P^{31} nucleus and that both the diamagnetic term and the terms contributed from other atoms could be neglected. Muller found that observed P^{31} chemical shifts should be correlated with bond properties using a semi-empirical equation of the type

$$\delta = a - bD$$

where D is the number of unbalanced p-electrons and a and b are empirical constants. The number of unbalanced p-electrons arises from an unequal distribution of electrons in the three p-orbitals. D can be calculated from considerations of the extent of hybridization and the degree of ionicity in the bonding atomic orbitals. From the data for PH_3 and PCl_3 the constants a and b were evaluated. The final relationship obtained was

$$\delta = 4.2 \times 10^2 - 1.2 \times 10^3\ D.$$

Parks[9] modified Muller's original equation and obtained a new expression for the chemical shift:

$$\delta = -230 + 29.0 \times 10^3 \exp(-46D')$$

where D' is still the number of unbalanced p-electrons but is calculated in a different manner. This modified equation allows for the fact that as the phosphorus hybridization approaches sp^3, the number of unbalanced p-electrons, D', approaches zero. Parks' modified equation seems to give better agreement with experimental results than does Muller's.

In contrast to this semi-empirical work, Letcher and Van Wazer[10,11,12,13] have carried out quantum-mechanical calculations of P^{31} chemical shifts in an attempt to explain available data. Their calculations considered s,p and d-orbitals and the possibility of both σ and π bonding.

Applications[1,2]

The use of P^{31} nmr has proven to be very helpful in structure determinations of inorganic phosphorus compounds. The structures of the various phosphate ions have been determined or verified by measuring their P^{31} resonances. This technique has helped to achieve some degree of order in the field of condensed phosphates. Phosphorus atoms in isolated, end, middle and branding phosphate groups each give rise to separate P^{31} resonances with characteristic chemical shifts.[25,26] The dialkylphosphonates have been shown by P^{31} nmr measurements to have the structure $(RO)_2P(H)O$ rather than $(RO)_2POH$. This was indicated by the large splitting due to the directly bonded hydrogen.

By using P^{31} nmr T. Moeller and P. Nannelli[23] determined that two isomers of the composition $P_3N_3(C_6H_5)_3Br_3$ were the cis-1,3,5 and trans-1,3,5 isomers. The spectrum of the cis compound consists of a single peak while that of the trans consists of two peaks with an intensity ratio of 2:1.

An interesting example is that of a solid sample of phosphorus penta-chloride.[24] This is one of the few samples to be examined by P^{31} nmr in the solid state. The presence of two different phosphorus species in the solid state, as indicated by two chemically shifted resonance peaks, supports the presence of two differently charged phosphorus moieties in the compound, namely $[PCl_6]^-$ and $[PCl_4]^+$. The removal of dipolar broadening was achieved by rotating the sample about an axis which makes an angle of 54° 44' with the direction of the applied field.

P^{31} nmr is also useful in the quantitative analysis of phosphorus containing compounds.[1] Two factors enable one to analyze mixtures of phosphorus containing compounds conveniently by nmr. First, most organophosphorus compounds contain only one phosphorus atom per molecule and thus have relatively simple spectra and second, the P^{31} resonances for different compounds usually have very different chemical shifts. Consequently, there is little tendency for the different absorption bands to overlap. Sensitivity factors limit the method considerably and it is difficult to conduct accurate quantitative measurements of resonance peak intensities if solutions of less than 1M concentration are used.

The compounds of triply connected phosphorus are commonly employed as ligands in transition-metal chemistry. At the present time only a few of the compounds have been studied by P^{31} nmr.[17-20, 27-32]

In 1961, Meriwether and Leto[17] reported the first P^{31} nmr study on metal complexes of phosphines. They measured the P^{31} chemical shifts of a number of nickel-carbonyl-phosphine complexes in an attempt to obtain a method for determining bond type in the complexes.

The various effects that may influence the chemical shift of phosphorus in the complexes were outlined in this paper. These effects are (1) a temperature independent paramagnetic contribution in the diamagnetic complexes, (2) formation of a donor σ-bond from P to Ni, (3) the contribution from dπ-dπ back donation

from nickel to phosphorus, (4) aromatic ring currents in the phenyl phosphines, (5) inductive effects of the phosphine substituents, (6) bond rehybridization effects due to changes in phosphorus bond angles upon complex formation, (7) electronegativity of the atoms joined to the phosphorus atom and (8) steric effects, including chelation. It was concluded that for the compounds studied the major contribution to the chemical shift is from the strong σ-bond from P to Ni and that any $d\pi$-$d\pi$ back donation from Ni to P was either very small or constant throughout the series.

Subsequent papers $^{18-20, 27-32}$ have dealt with the effects outlined by Meriwether and Leto and additional problems such as the influence of valency^{31} on the chemical shift or the effect of cis-trans isomerism on heavy metal-phosphorus coupling constants.^{18,19,24,29} The major portion of the work done up to date has been in the area of phosphorus-metal-carbonyl complexes.

Summary

From the above discussion, the utility of P^{31} nuclear magnetic resonance should be obvious. The most promising area for future work in this field is in the continued study of phosphorus-containing transition metal complexes. This study should include paramagnetic as well as diamagnetic complexes although the interpretation of chemical shifts in paramagnetic complexes would be difficult. Letcher and Van Wazer state that their theory of P^{31} chemical shifts can be modified to explain shifts in the paramagnetic complexes.^{13}

References

1. J. W. Emsley, J. Feeney and L. H. Sutchiffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, N.Y. 1965, Vol. 2, pp 1052-1078.
2. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance" McGraw-Hill, N.Y. 1959 pp. 346-356.
3. W. D. Knight, Phys. Rev., 76, 1259 (1949).
4. W. C. Dickenson, Phys. Rev., 81, 717 (1951).
5. N. F. Ramsey, Phys. Rev., 78, 699 (1950).
6. N. F. Ramsey, Phys. Rev., 86, 243 (1952).
7. N. Muller, P. C. Lauterbur and J. Goldenson, J. Am. Chem. Soc., 3557 (1956).
8. A. Saika and C. P. Slichler, J. Chem. Phys., 22, 26 (1954).
9. J. R. Parks, J. Am. Chem. Soc., 79, 757 (1957).
10. J. H. Letcher and J. R. Van Wazer, J. Chem. Phys., 44, 815 (1966).
11. " " " " " " 45, 2916 (1966).
12. " " " " " " 45, 2926 (1966).
13. "Topics in Phosphorus Chemistry", Vol. 5. Editors: M. Grayson and E. J. Griffith. Interscience Publishers, N.Y. 1967.
14. P. C. Lanterbur, "Determination of Organic Structures by Physical Methods," Vol. 2 Chap. 7, Ed. F. C. Rachod and W. D. Phillips, Academic Press, N.Y., (1962
15. J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, J. Am. Chem. Soc., 5715 (1956).
16. H. S. Gutowsky and D. W. McCall, J. Chem. Phys., 22, 162 (1954).
17. L. S. Meriwether and J. R. Leto, J. Am. Chem. Soc., 83, 3192 (1961).
18. A. Pidovik, R. E. Richards and L. M. Venanzi, Proc. Chem. Soc., 184, (1962).
19. " " " " " " J. Chem. Soc., (A), 1707, (1966).
20. S. O. Grim, David A. Wheatland, and W. McFarlane, J. Am. Chem. Soc., 89, 5573, (1967).
21. R. A. Y. Jones and A. R. Katvitzky, Angew. Chem., Int. Edn., 1, 32, (1962).
22. H. S. Gutowsky and J. Larmann, J. Am. Chem. Soc., 87, 3815 (1965).
23. T. Moeller and P. Nannilli, Inorg. Chem., 2, 659 (1963).
24. E. R. Andrew and V. T. Wynn, Pro. Roy. Soc., (London), Ser A, 291, 257 (1966).

25. J. P. VanWazer, C. F. Callis, J. N. Shoalery and W. A. Anderson, J. Am. Chem. Soc., 79, 2719 (1957).
26. J. R. VanWazer, L. F. Callis and J. N. Shoalery, J. Am. Chem. Soc., 4945 (1955).
27. S. O. Grim, W. McFarlane, and D. A. Wheatland, Inorg. Nucl. Chem., Letters, 2, 49 (1966).
28. S. O. Arim, and R. A. Ferince, ibid., 2, 205 (1966).
29. S. O. Grim, R. L. Keiter and W. McFarlane, Inorg. Chem., 6, 1133 (1967).
30. S. O. Grim, D. A. Wheatland, and P. R. McAllister, Inorg. Chem., 1, 161 (1967).
31. S. I. Shupack and B. Wagner, Chem. Commun., 547 (1966).
32. G. S. Reddy and R. Schmutzler, Inorg. Chem. 6, 823 (1967).

MAGNETIC DOUBLE RESONANCE

Jeffrey Zink February 27, 1968

I. Introduction

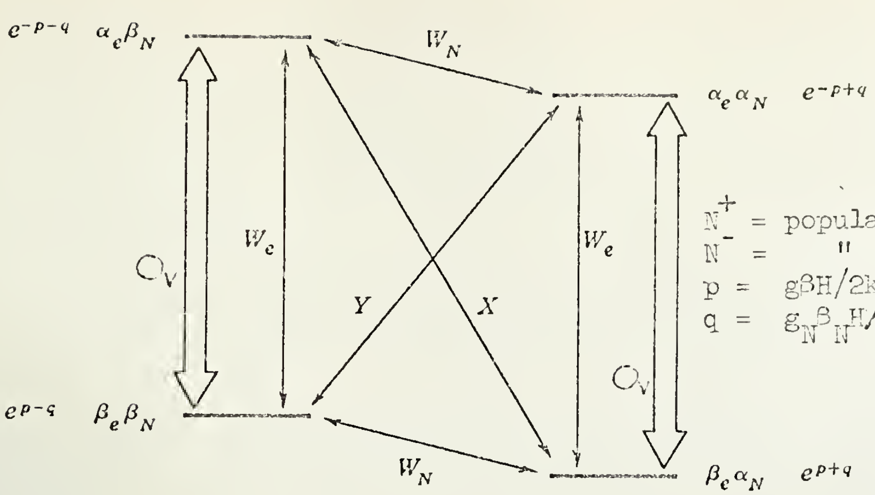
Double resonance refers to the general type of spectroscopic experiment in which a system is simultaneously irradiated at two different frequencies. In magnetic double resonance, transitions between nuclear or electron spin states in a magnetic field are studied using oscillatory magnetic fields of two different frequencies. Typically, these oscillatory fields are supplied by radio frequency or microwave electromagnetic radiation applied at right angles to the static magnetic field. Of the four types of such experiments which can be conceived, the following three are of particular interest to chemists. First, the molecule can be irradiated at a nuclear resonance frequency while other nuclear resonances are simultaneously observed. Second, nuclear resonances can be induced while electron resonances are observed. Finally, the molecule can be irradiated at the electron resonance frequency while nuclear resonances are observed. The first method is called Nuclear Magnetic Double Resonance (NMDR). The second and third methods are called Electron Nuclear Double Resonance (ENDOR), although the term ENDOR is generally applied to experimental methods of the second type.[1] The Overhauser effect may occur in the third method. This effect is manifested by large increases or decreases in the nmr signal intensity. If such a change occurs in NMDR, it is called a nuclear Overhauser effect.

The three magnetic double resonance techniques described above may all be explained by a general theory of double resonance. Important differences exist among the techniques which allow very different uses to be made of them. These differences occur both in the physical properties of the system under study and the experimental conditions applied. This seminar will describe the general theory of magnetic double resonance connecting the various techniques, delineate their characteristic differences, and describe the types of information of chemical interest obtainable from each.

II. Elementary Theory of a Two Spin System.

Since there is no difference in principle between the double resonance behavior of an electron-nuclear spin system and that of two nuclei, a discussion of the theory of any one of these techniques will lead to an understanding of the other.[1] Consider a system consisting of an unpaired electron ($S = 1/2$) and a proton ($I = 1/2$) coupled together by a time dependent contact hyperfine interaction $V(t) = a(t)\vec{I}\cdot\vec{S}$ with an average value of zero.[4] The ESR spectrum of this system will lack hyperfine structure, and the energy levels will correspond to the Zeeman Hamiltonian $H_o = g\beta HS_z - g_N\beta_N HI_z$. The populations of these levels (at thermal equilibrium) obey the Boltzmann distribution law. The spin levels and their relative populations are shown in the energy level diagram below.[1]

(See page 64)


e^{-p-q} $\alpha_e\beta_N$
W_N
$\alpha_e\alpha_N$ e^{-p+q}
O_V
W_e
Y
X
W_e
O_V
e^{p-q} $\beta_e\beta_N$
W_N
$\beta_e\alpha_N$ e^{p+q}

N^+ = population of α nuclear spin states
N^- = " " β " " "
$p = g\beta H/2kT$
$q = g_N\beta_N H/2kT$

These relative populations are maintained by various relaxation processes. Illustrated in the diagram are electron spin-lattice relaxation with transition probability W_e, nuclear spin-lattice relaxation with probability W_N, electron-nuclear relaxation with probability X, and double relaxation with probability Y. X arises from the time dependent scalar coupling and Y arises from dipolar coupling. The existence of these finite transition probabilities requires that the nuclear relaxation rate depends upon the populations of the electron states and leads to dynamic polarization and the Overhauser effect.[5,6]

The Overhauser effect occurs in the above cases if the electron spin resonance is saturated while a nuclear absorption line is observed.[7] This corresponds to saturating the electron spin such that the probability $O_v \gg W_e, X, Y$. The electron spin states then have equal populations. In the case where only scalar coupling operates, the balance between N^+ and N^- is maintained by X.[8,9] Hence $XN_{\alpha\beta}e^{-p+q} = XN_{\beta\alpha}e^{-p-q}$, where the N's refer to the populations of states with electron spin denoted by the first subscript and nuclear spin by the second. Thus, $N\beta\alpha/_{N\alpha\beta} = N^+/_{N^-} = e^{2p+2q}$. The difference between the nuclear α and β spin states has thus increased by a factor of $f = (1 + {}^{g\beta}/g_N\beta_N) = 659$, causing a nmr signal increase by the same factor. If, in addition, dipolar coupling is operative, the enhancement factor becomes $f = [1 + S\,\xi\,(g\beta/_{g_N\beta_N})]$ where $\xi = (X-Y)/_{(2W_N+X+Y)}$ and S is the degree of saturation.[1,10,11] Since scalar and dipolar coupling lead to opposite signs of ξ [9], studies of the types of magnetic coupling interactions are feasible by the double resonance method.

In the case where electrons and nuclei relax independently and hyperfine coupling is not zero, the nuclear spin populations may still be altered by saturating " forbidden" ESR transitions. Enhancement by this method is called the solid-state effect.[1,5]

The term ENDOR is applied to the technique in which pulses of radio frequency radiation are used to interchange the populations of nuclear spin states. As these pulses are swept through a suitable range of frequencies, sudden enhancements of ESR absorptions are observed.[1,5]

In addition to spin polarization effects in NMDR, collapse of spin multiplets may also occur. The origin of this "decoupling" is quite different from the collapse due to short relaxation times or chemical exchange.[12] It is incorrect to describe the collapse as arising from the saturation of the irradiated nucleus. The decoupling arises because the irradiated nucleus

is essentially quantized along the X axis while the observed nucleus is quantized along the Z axis.[2] Hence the term $J\vec{I}\cdot\vec{I}$ vanishes. The spectra may be explained theoretically using a coordinate system rotating with the frequency of the decoupling radiation. In this coordinate system the time dependence is treated as a perturbation. Using an appropriate complete set of basis functions, the frequencies and relative intensities of absorption may be calculated.[13,14]

III Applications

The most important and widely used applications of magnetic double resonance are enumerated below. Recent examples are included.

Overhauser Effect[7]

1. Studies of magnetic interactions in solution. Dweck, *et al.*,[15] investigated the Overhauser effect for solutions of 246 tri-tertbutyl phenoxy radical in organic solvents. The scalar interaction is best explained in terms of a diffusion model.

2. Enhancement of absorption signals of nuclei to which nmr is insensitive. Dweck and Richards [16] observed ^{31}P resonances enhanced a maximum of 50 times.

3. Enhancement of absorption signals of nuclei present in low isotopic abundance. Natusch, *et al.*,[17] observed ^{31}C in natural abundance. Both positive and negative enhancements were observed.

ENDOR

1. Measurement of hyperfine splittings under conditions where the lines overlap. Tagaya *et al.*, observed hyperfine interactions of O_3^- with ^{107}Ag and ^{109}Ag in a $AgNO_3$ lattice. Read and Whiffen [20] identified the $CH_3CHCOOH$ radical hyperfine lines in the presence of interfering absorptions.

2. Study of hyperfine structure of F centers. Holton, *et al.*,[21] resolved hyperfine interactions from ^{7}Li and ^{19}F nuclei up to 7 connection shells away.

NMDR

1. Spin decoupling.[2] Lippard, *et al.*,[22] showed that iron tricarbonyl cyclooctatetraene has the cyclooctatetraene bonded in the manner of a 1-3 diene. Many other examples of spin decoupling are found in the recent literature.

2. Determination of relative signs of coupling constants. McFarlane determined the signs of ^{29}Si - ^{1}H [23] and ^{14}N - ^{1}H [24] coupling constants in a variety of compounds. Deck [14] completely analyzed various fluorobenzenes and fluoropyridines.

3. Measurement of relaxation times. Rao and Lessinger [25] developed the theory of the effect of relaxation on NMDR spectra and experimentally compared the relaxation times of ^{19}F to ^{1}H in ethyl fluoride.

4. Elimination of quadrupole broadening. Randall, *et al.*,[28] removed the ^{14}N broadening in the ^{1}H spectrum of pyridine and compared the spectra to the theoretical one.

IV. Conclusion

The methods of double magnetic resonance are very powerful in elucidating magnetic molecular properties and interactions. With the exception of spin-decoupling experiments in NMDR, these methods are not widely used due to a scarcity of instruments. However, a great deal more information is often obtained from double resonance experiments than from the ordinary nmr or ESR experiment.

References

1. A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, (1967), pp. 229-240. An excellent introductory treatment.
2. J. D. Baldeschwieler and E. W. Randall, Chem. Rev., 63, 81 (1963).
3. C. D. Jeffries, Ann. Rev. Nuc. Sci., 14, 101 (1964).
4. P. S. Hubbard, Proc. Roy. Soc., A291, 537 (1966).
5. C. P. Poole, "Electron Spin Resonance", Interscience, New York, (1967), Chapter 19.
6. A. W. Overhauser, Phys. Rev., 89, 689 (1953).
7. L. G. Kent, Inorg. Chemistry Seminar, University of Illinois, 1967, pp.53-54 Contains a good list of references.
8. A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, (1961).
9. P. E. Richards and S. W. White, Proc. Roy Soc., A283, 459 (1965).
10. I. Solomon, Phys. Rev., 99, 559 (1955).
11. D. F. S. Natusch, R. E. Richards, and D. Taylor, Mol. Phys., 11, 421 (1966). Treatment of a three spin system.
12. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, London, (1965), pp. 240-248, 456-476.

13. H. G. Hecht, "Magnetic Resonance Spectroscopy," John Wiley and Sons, (1967) New York , Chapter 6.
14. J. C. Deck, Thesis, University of Illinois, 1966.
15. R. A. Dweck, J. C. Kentworthy, D. F. S. Natasch, R. E. Richards, and D. J. Shields Proc. Roy. Soc., A291, 487 (1966).
16. R. A. Dweck and R. E. Richards, Chem. Comm., 581 (1966).
17. D. F. S. Natasch and R. E. Richards, Ibid, 579 (1966).
18. R. A. Dweck, H. B. Hill, S. G. Kentworthy, D. F. S. Natasch, and R. F. Richards, Mol. Phys., 13, 27 (1967).
19. K. Tagaya and T. Nogato, J. Phys. Soc. Jap., 23, 70 (1967).
20. S. F. J. Read and D. H. Whiffen, Mol. Phys., 12, 159 (1967).
21. W. C. Holton, H. Blum, C. P. Slichter, Phys. Rev. Letters, 5, 197 (1960).
22. R. Gubbs, R. Breslow, R. Herber, S. J. Lippard, J. Am. Chem. Soc., 89, 6864 (196
23. W. McFarlane, J. Chem. Soc., A8, 1275 (1967).
24. W. McFarlane, Ibid, A10, 1660 (1967).
25. B. D. Nageswara Rao and C. Lessinger, Mol. Phys., 12, 221 (1967).
26. P. S. Hubbard, J. Chem. Phys., 42, 3546 (1965).
27. W. P. Unruh and J. Culvahouse, Phys. Rev., 129, 2441 (1963).
28. W. Randall and J. D. Baldeschwieler, Proc. Chem.Soc., 303 (1961).
29. H. Ward and R. G. Lawler, J. Am. Chem. Soc., 89, 5518 (1967).
30. H. Ward and R. G. Lawler, Ibid, 89, 5519 (1967).

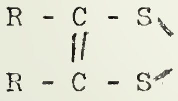
TRIS DITHIOLATE COMPLEXES --

TRIGONAL PRISMATIC COORDINATION

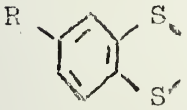
Glenn C. Vogel March 28, 1968

Introduction

Independent reports in 1962 of the complexes Ni $[S_2C_2(C_6H_5)_2]_3$ and Ni$[S_2C_2(CN)_2]_3^{-2}$ have stimulated great interest in coordination chemistry for this type of bidentate ligand. Some of the ligands that have been investigated are:



R = H, CN (m nt), C_6H_5(Sdt), CF_3, CH_3, P-$C_6H_4CH_3$, p-$C_6H_4OCH_3$



R = CH_3 (tdt), H (bdt)

With the late transition metals, these ligands form very stable square planar complexes. Polarographic studies have shown that this planar stereochemistry is unchanged in several oxidation states. [1]

Schrauzer and coworkers extended the studies of complexes with this type of ligand to the early transition metals in an attempt to obtain square planar bis complexes of metals which lie to the left of the periodic table. They reported bis complexes of V, Cr, Mo, W, Re, Ru, and Os. [2] Closer study of these complexes showed that they were not the unusual four-coordinate complexes, but instead six-coordinate. In this seminar the six-coordinate tris complexes will be discussed.

Preparation

The first well-characterized tris dithiolate complex was prepared by R. B. King in 1963. [4] The complex $[Mo\,S_6C_6(CF_3)_6]$ was prepared by the reaction of molybdenum hexacarbonyl with bis(trifluoromethyl)-1,2-dithietene. A. H. Maki and coworkers extended the preparation of neutral complexes with this ligand to other metals and in addition prepared the corresponding mono- and dianion. [5] For the dianion

$$[MS_6C_6(CF_3)_6] + [(C_6H_5)_4N]Cl \xrightarrow[\text{ethanol}]{\text{hydrazine}} [(C_6H_5)_4N]_2[MS_6C_6(CF_3)_6]$$

For the monoanion

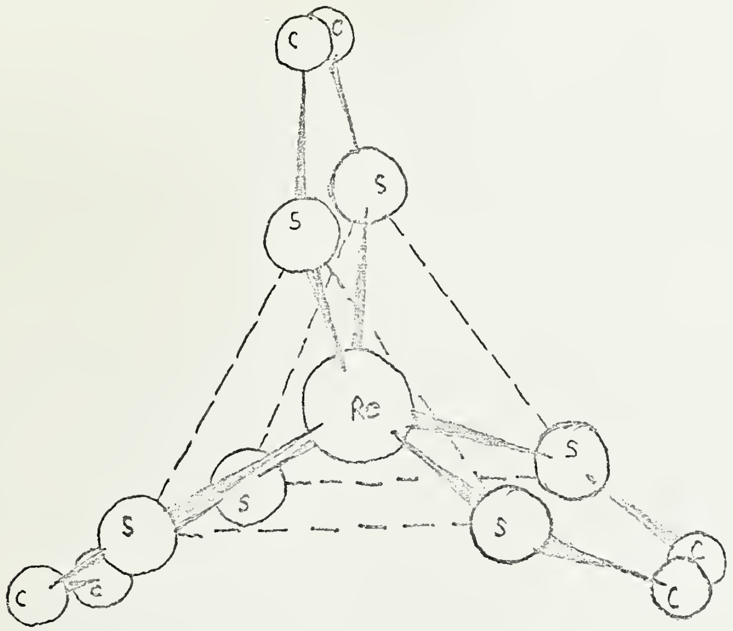
$$[MS_6C_6(CF_3)_6] + [MS_6C_6(CF_3)_6]^{-2} \longrightarrow 2[MS_6C_6(CF_3)_6]^-$$

G. N. Schrauzer and coworkers developed a general method for the preparation of transition metal complexes of the dithio-α-diketones $M(S_6C_6R_6)$ which uses the easily accessible acyloins and P_4S_{10} for the synthesis.[6] This method of preparation has been successful for all R- groups investigated except R = H or CN. In these latter cases, the sodium salt of the dithiolate $Na_2[S_2C_2R_2]$ is used.

Stiefel and Gray synthesized the tris (toluene-3,4-dithiolato) and tris (benzene-1,2-dithiolato) complexes.[7] These complexes were formed by the reaction of the metal chlorides with the corresponding dithiol.

Stereochemistry

Since the brilliant work of Alfred Werner, the maxim "six coordination equals octahedral complex" has been supported by countless structural determinations. Exception to this maxim was revealed with the X-ray structural investigation of tris(cis 1,2-diphenylethane-1,2-dithiolate)rhenium, $Re(Sdt)_3$.[8] In this molecule, rhenium was found to be surrounded by six equidistant sulfur atoms in a trigonal prismatic coordination. A perspective drawing of the coordination geometry excluding the phenyl rings is shown below:



The sides of the prism are nearly perfect squares with an average edge length of 3.043 Å. The five membered chelate rings lie in a plane and radiate out from the three-fold symmetry axis in a "paddle wheel" fashion. The phenyl rings (not shown on the drawing) are twisted out of the plane defined by the five membered chelate ring. The closest Re-Re distance is approximately 9.5Å.

Comparison of solid state and solution properties of $Re(Sdt)_3$ showed that trigonal prismatic coordination is maintained in solution. Similarity between the properties of $Re(Sdt)_3$ and $Re(tdt)_3$ confirmed the "non-classical" structural for the latter.[7]

Additional X-ray-structural determinations showed $Mo[S_6C_6H_6]$ and $V(Sdt)_3$ to possess this unusual geometry.[9,10] Isomorphism, as established by X-ray powder measurements, and gross similarity in the electronic spectra have been utilized to extend our knowledge of this unusual geometry to other complexes.[11]

Three structural determinations on the prismatic complexes and six structural determinations on the square planar complexes containing these bidentate

sulfur donor ligands have revealed an interesting and significant fact. Regardless of the central metal atom or the coordination geometry (square planar or trigonal prismatic) the S-S distance always is found to be near 3.05Å. This suggests that there are interligand bonding forces present.

Observations

Polarographic studies have been carried out on the tris complexes and it has been shown that the six coordinate species are stable over several oxidation states. The half-wave potentials depend on the ligands in a similar manner as in the case of the bis dithiolate complexes. Both types of complexes exhibit a linear correlation between the half-wave potential and the Taft inductive parameter.[12]

Comparison of nmr spectra of the sodium salt of the ligand $[S_2C_2H_2]$ with that of the coordinated ligand indicates "aromatic" character in the five membered chelate ring. Additional proof of the "ring current" was obtained by a Friedel-Crafts alkylation of $Mo(S_6C_6H_6)$.[13]

Bonding Schemes

At the present time two molecular orbital schemes are given in the literature. Both models describe the bonding in the trigonal prismatic complexes as "delocalized". However, the molecular orbital energy level orderings do not agree. The main difference in the two calculations appears to be the value of the diagonal Hamiltonian matrix elements chosen for the ligand.[11,13]

In addition, a stabilizing σ-interaction of the e^1 molecular orbital has been proposed as an explanation of the stability of the trigonal prismatic geometry.[14]

Prospective

No generality of the geometry of the tris dithiolate complexes as a function of metal and charge has been established. The recent report [15] that $[V(mnt)]^{-2}$ has only C_2 symmetry leads to the speculation that charge may play an important role in determining the stereochemistry of the complex, the oxidized form possessing trigonal prismatic coordination while the more highly reduced forms approach octahedral symmetry. It is evident that more X-ray studies are needed in this field.

References

1. H. B. Gray, Coord. Chem. Reviews, 1, 156 (1966).
2. G. N. Schrauzer, V. P. Mayweg, H. W. Finck, U. Miller, Westerhoff, and Heinrich, Angew. Chem. Intern. Ed. Enyl. 3, 381 (1964).
3. G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, Angew. Chem. Intern. Ed., Engl., 3, 639 (1964).
4. R. B. King, Inorg. Chem. 2, 641 (1963).
5. A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, J. Am. Chem. Soc., 86, 2799 (1964).
6. G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, Inorg. Chem. 4, 1615 (1965).
7. E. I. Stiefel and H. B. Gray, J. Am. Chem. Soc., 87, 4012 (1965).
8. R. Eisenberg, and J. H. Ibers, J. Am. Chem. Soc., 87, 3776 (1965).
9. A. E. Smith, G. N. Schrauzer, V. P. Mayweg, W. J. Heinrich, J. Am. Chem. Soc., 87, 5798 (1965).
10. R. Eisenberg and H. B. Gray, Inorg. Chem. 6, 1844 (1967).
11. E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and H. B. Gray, J. Am. Chem. Soc., 88, 2956 (1966).
12. D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, J. Am. Chem. Soc., 88, 4876 (1966).
13. G. N. Schrauzer and V. P. Mayweg, J. Am. Chem. Soc., 88, 3235 (1966).

14. M. Gerlock, S. F. A. Kettle, J. Locke and J. A. McCleverty, Chem. Commun. 1966, 29.

15. E. I. Stiefel, Z. Dori, H. B. Gray, J. Am. Chem. Soc., 89, 3353 (1967).

STEREOCHEMISTRY AND BONDING IN EIGHT COORDINATE COMPLEXES

Lew Mykola Hryhorczuk

April 2, 1968

Introduction

In recent years it has become apparent that coordination number eight is much more prevalent than was previously thought. X-ray analysis has shown that many compounds whose stoichiometry does not suggest octacoordination actually have a crystallographic coordination number eight in the solid state. With the advancement of our knowledge of metal to metal bonding, it has been found that certain atoms in some cluster compounds, containing bridging ligands and metal to metal bonds, exhibit a coordination number eight.[1] The preparations of new ligands and the investigation of complex formation of the less familiar elements has still further increased the number of discrete molecular eight coordinated complexes. In this seminar, factors influencing the stability of octacoordination, structures and stereochemistry associated with coordination number eight, and the bonding that is involved will be discussed.

Factors influencing the stability of coordination number eight.

The nature of the central atom and the nature of the ligand are the two primary factors that influence the stability of coordination number eight, although other factors have been observed. Clark, et al.,[2] have pointed out that for the early transition series it is necessary that the central atom have a small number of d electrons, a high formal charge, and small energy differences between the (n-1)d, ns, and np orbitals. In order to prevent excessive polarization of the ligands and to minimize ligand-ligand repulsions, Parish[3] indicated that a delicate balance between the size and the charge on the central ion must be maintained. It was also suggested, that for complexes with a few d electrons, the dodecahedral and the Archimedean antiprismatic structures gain crystal field stabilization energy over the octahedron, tetrahedron, square plane and other regular structures.[4, 5, 6] Since eight ligands must surround the central atom, the size of the donating atoms, as pointed out by Muetterties and Wright,[7] is another important factor in eight coordinate complexes. The ability of a ligand to form chelate rings helps in stabilizing coordination number eight, especially if the multidentate ligand is compact. Orgel[5] predicted that π bonding between four ligands and a central ion with one or two d electrons will help to stabilize the dodecahedral structure.

Hoard and Siverton[8] observed that the solid compounds Na_3TaF_8, K_2TaF_7 and $CsTaF_6$ containing octa-, hepta-, and hexa- coordinated tantalum are obtained from solutions which differ only in the choice of the cation. Raman spectroscopy[9] of tantalum (V) in a HF - NH_4F - H_2O system revealed that no $[TaF_8]^{3-}$ was present. Using the same procedure in every case, Hargreaves and Peacock[10, 11] prepared K_3WF_8 and $NaWF_6$; K_2MoF_8, $RbMoF_7$, and $CsMoF_7$. Apparently, differences in crystal packing forces cause the stability of some eight coordinated anions to be dependent on the accompanying cation.[8]

Structure, Stereochemistry and Bonding.

Seven different structures have been proposed for eight coordinate complexes. These are: The cube,[12, 13] the Archimedean antiprism,[14] the

dodecahedron,[15] the undecahedron (a trigonal prism with two extra bonds on the rectangular faces) [15], the trigonal prism with two extra bonds along the C_3 axis [16], the hexagonal bipyramid [17], and the bicapped trigonal antiprism. [18, 19] The square antiprismatic structure has been discussed in detail by Hoard and Silverton. [8] This type of arrangement has been observed in complexes of monodentate ligands: $Na[TaF_8]$ [20] and $K_2[ReF_8]$ [21]; bidentate ligands: $[Th(acac)_4]$ [22] and $[Zr(acac)_4]$ [23]; and polymeric complexes: $Ce(IO_3)_4$ [24], $Zr(SO_4)_2 \cdot 2H_2O$ [25], and $Zr(IO_3)_4$ [26]. Hoard and Nordsieck [15] first reported that the $[Mo(CN)_8]^{4-}$ ion has a dodecahedral configuration. Isostructural with it are the $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$ and $[W(CN)_8]^{3-}$ ions. This structure also has been observed in complexes with bidentate ligands: $Na_4[Zr(C_2O_4)_4] \cdot 3H_2O$ [27, 28], $[Ce(C_6H_5COCHCOC_6H_5)_4]$ [29], $[Ti(diars)_2Cl_4]$ [30] which is isostructural with $[V(diars)_2Cl_4]$, $[Zr(diars)_2Cl_4]$ and $[Hf(diars)_2Cl_4]$ [30], $Cs[Y(CF_3COCHCOCF_3)_4]$ [31] $NH_4[Pr(CF_3COCHCOC_4H_3S)_4] \cdot H_2O$ [32], the $[Co(NO_3)_4]^{2-}$ ion [33], and $K_3[CrO_8]$ [34a, 34b]. In $K_2[Zr(N(OAc)_3)_2] \cdot H_2O$ the nitrilotriacetate ion is a quadridentate ligand [35]. Some polymeric complexes exhibiting dodecahedral structure are K_2ZrF_6 [36] and $Zr(OH)_2(SO_4)_3(H_2O)_4$ [37]. The uranyl (UO_2^{2+}) type ion can coordinate to six other ligands forming the planar and the puckered hexagonal bipyramidal structures. For $[UO_2(NO_3)_2(H_2O)_2] \cdot 4H_2O$ a configuration of hexagonal bipyramid was observed.[17] In $Na[UO_2(O_2CCH_3)_3]$ [39] and in $Rb[UO_2(NO_3)_3]$ [40] a small amount of puckering in the hexagon has been reported. In polymeric compounds $Ca(UO_2)O_2$ [19] and UO_2F_2 [18] a large amount of puckering has been observed. No structures of the type suggested by the trigonal prism with two extra bonds along the principal axis, the cube, or the undecahedron have been reported.

The preference of one configuration over others in eight coordinated complexes is dependent on many factors. The planar and the puckered hexagonal bipyramidal structures, as indicated by Kepert, [38] are stabilized by the presence of two short metal to ligand bonds which results from the special bonding that exists in the UO_2^{2+} ion. The ligand-ligand repulsions and the constraints of the bidentate ligands are probably two of the factors which influence the puckering of the hexagon. Hoard and Silverton [8] list four points which they believe have significant influence on the stabilization of the dodecahedral and the square antiprismatic structures with respect to each other and the cubic configuration. These are: 1) The bonding between the central atom and its ligands, 2) the mutual repulsion of the ligands, 3) the effect of non-bonding electrons in the valence shell, and 4) the constraints due to bidentate and multidentate ligands.

1) The Bonding

By symmetry group considerations of the cube, Van Vleck [41] has shown the possible hybridizations are d^3sp^3f and d^3sf^4. By a similar use of the symmetry involved, Kimball [42] has shown that for a square antiprism, two sets of hybridized orbitals are possible: d^4sp^3 and d^5p^3. For the dodecahedron only d^4sp^3 hybridization is possible and for the undecahedron the possibilities are d^4sp^3, d^5p^3 and d^5sp^3. However, he did not consider the f orbital symmetries in these cases. Szirmazan and Dyatkina [43] did take into account the possibility of f orbital participation in the hybridization and derived an additional 26 sets of possible hybrid orbitals for the dodecahedron and 41 for the undecahedron. Racah [44] determined that s-p-d

hybrid bonds, directed to the corners of an Archimedean antiprism and making an angle of 60° 54' with the principal axis, have a bond strength of 2.9886 in comparison with 3.0, the maximum possible bond strength. The maximum bond strength of 2.988 was calculated for a $s^{0.9}\ p^3\ d^{4.1}$ hybrid by Duffey.[45] The critical angle in the antiprismatic structure with this hybridization is 60° 54'. For sp^3d^4 hybrid orbitals the bond strength is 2.979 and the angle is 57° 35'. For the dodecahedral structure, Racah[44] divided the eight bonds into two sets of four equivalent hybrid orbitals. He showed that one set of orbitals, which make an angle of 34° 33' with the unique two-fold axis, has a bond strength of 2.9954, and the other set, which makes an angle of 72° 47', has a bond strength of 2.9676. Duffey[46] related the maximum bond strengths to the hybridization in the two sets of orbitals which were expressed as $s^n p^{3m} d^{4-n-3m}$ and $s^{1-n}\ p^{3-3m}\ d^{n+3m}$. The total hybridization of sp^3d^4 has one set of hybrid orbitals having an s content of 0.1042, a p content of 0.3542 and a d content of 0.5416, and another set having an s content of 0.1458, a p content of 0.3958 and a d content of 0.4584.

On the basis of these calculations, it is concluded both for the square antiprism and for the dodecahedron, that the hybridization is sp^3d^4. The possible bond strength of 2.9886 to 2.979 for the antiprism compared with the average bond strength of 2.9815 for the dodecahedron shows that this criterion does not exhibit preference of one structure over the other.

2) Ligand-Ligand Repulsions.

Several researchers[8, 38, 47] have considered the effect of ligand-ligand repulsions. The repulsion energy, V, is proportional to the sum of r^{-n} where r is the distance between the various ligands, and n is the Born coefficient.[48]

$$V = k \sum \frac{1}{r^n}$$

The summation is carried out over all twenty-eight ligand-ligand separations. Parish and Perkins[47] calculated the repulsion energies, as a function of the critical angles, by assuming a constant metal to ligand distance, arbitrarily chosen as one, and by assuming a rigid molecule without distortions. From their published figures, it is concluded that for the electron donating atom with a Ne like electron configuration, such as N, O, and F, the n value is 7 and the antiprismatic structure is prefered by 1.69% over the dodecahedral configuration if no shielding is involved. With the use of different shielding parameters the antiprism is more stable by about 1.21 - 2.12%. Because these differences are so small, no significant prediction can be made as to which of the two structures is more stable.

3) The effect of Non-Bonding Valence Shell Electrons.

Parish[49] pointed out that the non-bonding valence shell electrons either stabilize a particular structure by π bonding and by giving rise to crystal field stabilization energy, or distabilize it through electron-ligand repulsions. Orgel[5] argued that in the dodecahedral structure the presence of electrons in a non-bonding orbital causes π bonding which stabilizes this configuration. On the other hand, Hoard and Silverton[8] believe that in this structure the presence of non-bonding electrons actually loosens the σ bonding to such a degree that π bonding cannot compensate for it. Reporting just the conclusions based on calculations of group overlap integrals, Parish[50] states that the π bond strengths of dz^2 and dx^2-y^2 orbitals are in the ratio

of 1:1.4. In the dodecahedral structure the overlaps of the dx^2-y^2 orbital with atoms at A and B positions are in a ratio of 1 to 1.63. In general, no conclusion can be reached concerning the preferred configuration.

4) The Effect of Multidentate Ligands.

The formation of geometrical constraints in chelate rings is an important factor that may determine which configuration is the more stable. [8] The dodecahedral structure has a great variety of edges (a, b, g, m) which the ligand can span, whereas the antiprism has only two types of edges (s, l). This, of course, gives the dodecahedron a slight advantage since the chelating ligand will have more choices as to which edges it will span. Also, the dodecahedron, having A and B positions with different possibilities of π bonding would be better able to accommodate chelate ligands with different donor atoms. Although these arguments are only qualitative, a study of tables V and VI [51], presented by Lippard, shows that, up to now, for non-polymeric species, antiprismatic structures are formed only by complexes of acetyl acetone (and in one case by the thenoyltrifluoroacetone). At least nine different chelating ligands coordinate in a dodecahedral structure.

Since no prediction can be made as to the stabilities of the dodecahedral and antiprismatic configurations of unidentate ligands, studies to determine the structures of octocyanato complexes in solution have been carried out. Stammreich and Sala [52, 53] observed that the Raman spectra of $K_4[Mo(CN)_8]\cdot 2H_2O$ in aqueous solution consists of three peaks which they were able to interpret in terms of D_{4d} (square antiprismatic) symmetry. Simultaneously but independently, König [54] and Golding and Carrington [55] published results on the electronic spectra of octacyanato complexes which the former researcher explained in terms of the D_{4d} symmetry and the latter investigators in terms of D_{2d} (dodecahedral) symmetry. Reflection spectra of $K_4[Mo(CN)_8]$, $K_4[Mo(CN)_8]\cdot 2H_2O$ and $K_4[W(CN)_8]\cdot 2H_2O$ which were determined by König were similar to the solution spectra and thus there was some question presented as to the validity of the crystalographic results. Perumareddi, Liehr and Adamson [56], shortly thereafter, reported their electronic spectra for the $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{-3}$, $[Mo(CN)_8]^{-4}$, $[W(CN)_8]^{4-}$ and $[Re(CN)_8]^{3-}$ ions which they interpreted in terms of Cs symmetry resulting from a slight distortion of the dodecahedron. A completely different conclusion was reached simultaneously by two independent researchers. On the basis of ESR studies both Hayes [63] and McGarvey [64] concluded that in solution $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ are in the antiprismatic configuration. Hayes determined his spectra in a methyl alcohol glass while McGarvey obtained spectra from a water solution, a glycerine glass and solid $K_4[Mo(CN)_8]$ doped with $K_3[Mo(CN)_8]$ and $K_4[W(CN)_8]$ with $K_3[W(CN)_8]$. The infrared spectroscopic investigation of the $[W(CN)_8]^{4-}$ ion by Parish [65] and of the $[Mo(CN)_8]^{4-}$ ion by Kettle and Parish [66] revealed that in the solid state the spectra could be interpreted in terms of a distorted D_{2d} configuration (Cs symmetry). In solution state only one broad peak was observed for each ion; this could not be correlated to any of the structures under consideration. In an attempt to resolve the discrepencies in the interpretation of the electronic spectra and the ESR experiments, Muetterties [68] reported that a single sharp peak was obtained in a C^{13} nmr study of the $[Mo(CN)_8]^{4-}$ ion enriched in C^{13}. Although, in his view, the results were consistent with an antiprismatic structure in which all CN^- ions are equivalent or with a dodecahedral structure which could have a very small chemical shift between

non equivalent ions, he believes that the most realistic explanation results from assuming rapid intramolecular exchange of the cyanide groups. To explain the stereochemistry in solution he suggests that potential energy surfaces be drawn showing the energies of various configurations. A suggested qualitative diagram of energy versus the shape function of the molecule is presented by Muetterties and Wright. [69]

It should be noted that crystal field splittings of the orbitals for the Archimedean antiprism [57, 58] and for the dodecahedron [59, 60, 61, 62] were reported earlier. The results for the antiprism agree; the dz^2 orbital has the lowest energy level followed by the doubly degenerate d_{xy} and dx^2-y^2 The degenerate d_{xz} and d_{yz} orbitals have the highest energy. For the dodecahedron, the orbital arrangement was somewhat confused. Parish and Perkins [47], who calculated the crystal field energies as a function of the dodecohedral critical angles, give the following orbital arrangement at $\theta_B = 36°$ and $\theta_C = 70°$ which are close to the crystalographic ($\theta_B = 36°$, $\theta_A = 71.8°$) values of $K_4[Mo(CN)_8]$: $b_1(dx^2 - y^2)$ $b_2(dxy)$ $a_1(dz^2)$ $e(dxz, dyz)$.

The stereochemistry of octacoordinate complexes becomes more intriguing when one considers the theoretical possibilities of isomers that could arise from the use of mixtures of monodentate ligands, mixtures of multidentate ligands, and mixtures of multidentate and monodentate ligands. Marchi, Fernelius and McReynolds [70] considered this problem and, by the use of equations developed by Lunn and Senior [71], were able to calculate the number of possible optically active and inactive isomers for the cubic, the dodecahedral, the square antiprismatic and the trigonal prismatic (two extra bonds along the C_3 axis) configurations. Lippard [72] has calculated the number of possible isomers of the hexagonal bipyramid and the puckered hexagonal bipyramid. In view that different numbers of isomers were calculated for different structures, Marchi and McReynolds [73] attempted to determine the structure of $K_4[U(C_2O_4)_2]$ by isolating and counting the various isomers. By fractional precipitation of the strychnine salt they found four optically active isomers. Johnson and Larsen [74] attempted to repeat the experiment and to expand the method to oxalate complexes of Zr(IV), Hf(IV) and Th(IV), but were unsuccessful. They report that oxalate exchange studies with labelled carbon showed that the ligands were labile so that exchange occurred within a few minutes. This rapid exchange of bidentate ligands in solution was also observed by Cotton, Legzdins, and Lippard [75] who studied a mixture of $[Y(CF_3COCHCOCH_3)_4]^-$ ion and $[Y(CF_3COCHCOCF_3)_4]^-$ ion in solution with nmr. At -40°C they obtained eight peaks for the unique hydrogen indicating that ligand exchange occurred and that 5 complexes Ya_4^-, Ya_3b^-, $Ya_2b_2^-$, Yab_3^-, and Yb_4^- were formed. At 40°C, only two peaks were observed for the unique proton, each associated with the particular ligand, and the spectrum was explained in terms of intermolecular ligand exchange.

In view of more recent developments in the stereochemistry of complexes with four bidentate ligands it is worthwhile to pursue the topic further. Hoard and Silverton [8] have demonstrated that for square antiprismatic structures with four symmetrical bidentate ligands one could obtain three optically active structures of symmetries D_4, D_2 and C_2. In the dodecahedral configuration, due to chelation along various edges, isomers of D_{2d}, S_4, D_2,

C_2 and C_1 symmetries are possible. For the tetrakis coordinated square antiprismatic configuration only the structure with D_2 symmetry is reported. The compounds $[Th(CH_3COCHCOCH_3)_4]$ [22] and $[Zr(CH_3COCHCOCH_3)_4]$ [23] exhibit this structure. For the dodecohedral arrangement, the only structures known for some time, were those with D_{2d} symmetry. Examples of this structure are the $[Zr(C_2O_4)_4]^{4-}$ and the $[Hf(C_2O_4)_4]^{4-}$ ions. [27, 28] Recent crystallographic investigation of $Cs[Y(CF_3COCHCOCF_3)_4]$ by Lippard, Cotton and Legzdins [31] and the investigation of $NH_4[Pr(CF_3COCHCOC_4H_3S)_4]$ by Lalancette, et al., [32] revealed that in these complexes D_2 (dodecahedral) and S_4 symmetries exist.

Two groups of researchers, Bauer, Blanc, and Ross,[76] and Brecher, Samuelson and Lempicki [77] investigated the fluorescent properties of octacoordinated complexes of the rare earth metals. Both groups assign emission energies in the range of 6100 - 6250 Å to the $^5D_0 \longrightarrow {}^7F_2$ transitions. On the basis of the electronic dipole selection rules, they predict various numbers of allowed transitions for different symmetries. These are: D_4-one, D_2-three, C_2-five, D_2d-two, S_4-three, and C_{2v}-four. By counting the number of peaks in the 6100-6250Å region, these researchers predicted various structures on the basis of the fluorescence spectra. By such a peak count Brecher, et al., [77] assigned D_2d symmetry to $[Eu(C_6H_5COCHCOC_6H_5)_4]^-$ ion but a D_2 symmetry to the $[Eu(CH_3COCHCOCH_3)_4]^-$ ion. Bauer, et al., [76] were able to obtain in the solid state two forms of the piperidinium salt of the $[Eu(C_6H_5COCHCOC_6H_5)_4]^-$ ion and of the corresponding gadolinium ion. The fluorescence spectra of one europium isomer at 78°K consisted of a triplet (D_2 or S_4) while that of the other was a doublet (D_2d). However, the azobicyclononane salt of $[Eu(C_6H_5COCHCOC_6H_5)_4]^-$ ion under the same conditions yielded a fluorescence spectrum consisting of five emission bands which suggested a C_2 symmetry.

For the hexagonal bipyramid and the puckered hexagonal bipyramid a number of isomers are possible. However, there has been little investigation of these. Nevertheless, one point can be made. For compounds of the type $[UO_2(AA)_2a_2]$ the trans configuration (by numbering around the hexagon, positions 1,2 and 4,5) apparently is more preferred than the cis (1,2 and 3,4) configuration. $[UO_2(NO_3)_2(H_2O)_2]$ [17] has been shown by crystallographic studies to be in a trans configuration.

The bonding in the hexagonal bipyramid complexes is interesting but difficult to explain. In general, on the basis of different bond lengths, it is believed that two different types of bonding exist; one type between the uranium and the apical oxygens and the other between the uranium and the ligands in the hexagonal plane [78]. Coulson and Lester [78a] carried out classical valence bond calculations under D_6h symmetry for the ligands in the hexagonal plane. These authors believe that here the actual hybridization is sp^2d^2f. For the D_3h symmetry, where a bidentate ligand (AA) is used, and the angle A-M-A in the chelate ring is less than 60°, there is a greater contribution of f character to the hybrid bonds and less of the s character. A series of papers has been written on the bonding in the uranyl part of the complex, but a recent critical review article by Dyatkina and Michailov [79] studied this more thoroughly. The recent review by Narasimhan [80], however, is qualitative and not as involved as the previous article. Since the uranium atom in addition to six valence electrons has a fairly large number of unoccupied orbitals in the 6d and 5f subshells, and since there are compounds in which a single oxygen atom is bonded by as many as four bonds, Dyatkina and Michailov favor triple bonds between the uranium and the uranyl oxygens. The third bond is formed by the donation of a lone pair on the oxygen to an empty orbital of uranium. This model was obtained independently on qualitative arguments by Dytkina, et. al., [81] and on the basis of a molecular orbital treatment by McGlynn and Smith [82, 83]. The

latter researchers calculated the approximate energies of the molecular orbitals and arranged them according to energy as $1\sigma_u^+ < 1\sigma_g^+ < 1\pi_u < 1\pi_g < \phi_u < \delta_u < 2\pi_u < 2\sigma_u^+$. For the UO_2^{2+} ion twelve electrons must be placed into the molecular orbitals. The bonding $[(1\sigma_u^+)^2 (1\sigma_g^+)^2 (1\pi_u)^4 (1\pi_g)^4]$ orbitals accommodate these electrons, giving a total of six bonds (three per oxygen). These derived molecular orbitals of the uranyl group are then subjected to a $D_{6}h$ distortion and then interact with the ligand orbitals to give a total molecular orbital diagram for this type of compound.

Other interesting questions on the bonding in complexes which may show the coordination number eight arise in connection with ions such as $[Co(NO_3)_4]^{2-}$ and $[CrO_3]^{3-}$. Straub, Drago, and Donoghue [84] on the basis of spectral and magnetic data, suggested a tetrahedral arrangement of ligands in the $[Co(NO_3)_4]^{2-}$ ion. Cotton and Bergman [85] determined the structure of this ion by X-ray diffraction and concluded that eight oxygens show bonding interactions. On chemical basis, Addison, et al., [86] noted that the unidentate nitrate ions are not reactive, whereas the bidentate nitrate groups possess strong oxidizing powers. In a reaction it is assumed that a bidentate nitrate would have to go through a unidentate state before it broke away from the complex. However, if the nitrate ion was bonded through a three center bond, it could break away in a single step. This would explain a tetrahedral ligand field around the cobalt in the $[Co(NO_3)_4]^{2-}$ ion. In support of this, they state that $[Sn(NO_3)_4]$, which has "bidentate" bonding, loses its reactivity when it becomes converted to $[Sn(NO_3)_4 \cdot 2py]$ in which all groups are unidentate. Three center bonds have also been suggested for complexes such as $[Ti(NO_3)_4]$ and $Mg_3[Ce_2(NO_3)_{12}] \cdot 2H_2O$ [87] and for $[Co(O_2CCF_3)_4]^{2-}$ [85]. Although Swalen and Ibers [88] investigated the perchromate ion in terms of ligand field calculations as a function of the dodecahedral symmetry, Tuck and Walters [89] suggest three center bonds and Cotton and Bergman [85, 87] suggest bonding similar to that in the $[Co(NO_3)_4]^{2-}$ ion.

Complexes of coordination number eight offer many interesting structures; this leads to a very rich stereochemistry and isomerism, and the problems associated with them. The various bonding schemes are still in question and more data associated with sophisticated calculations will give a greater insight into this problem.

References

1. E. L. Muetterties and C. M. Wright, Quart. Rev., 21, 151 (1967).

2. R. J. H. Clark, D. L. Kepert, R. S. Nyholm, and J. Lewis, Nature, 199, 559 (1963).

3. R. V. Parish, Coord. Chem. Rev., 1, 443 (1966).

4. J. S. Griffith and L. E. Orgel, Quart. Rev., 11, 381 (1957).

5. L. E. Orgel, J. Inorg. Nucl. Chem., 14, 136 (1960).

6. R. V. Parish, O. P. Cit., p. 444.

7. E. L. Muetterties and C. M. Wright, J. Am. Chem. Soc., 86, 5132 (1964).

8. J. L. Hoard and J. V. Silverton, Inorg. Chem., 2, 235 (1963).

9. O. L. Keller, Jr., and A. Chetham - Strode Jr., Inorg. Chem., 5, 367 (1966).

10. G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 1958, 2170.

11. G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 1958, 4390.

12. G. T. Morgan and H. W. Moss, J. Chem. Soc., 105, 189 (1919).

13. P. Pfeiffer, Z. Anorg. Chem., 105, 26 (1919).

14. G. F. Huttig, Z. Anorg. Allgem. Chem., 114, 25 (1920).

15. J. L. Hoard and H. H. Nordsieck, J. Am. Chem. Soc., 61, 2853 (1939).

16. L. E. Marchi, W. C. Fernelius and J. P. McReynolds, J. Am. Chem. Soc., 65, 329 (1943).

17. J. C. Taylor and M. H. Mueller, Acta Cryst., 19, 536 (1965).

18. W. H. Zachariasen, Acta Crys., 1, 277 (1948).

19. W. H. Zachariasen, Acta Cryst., 1, 281 (1948).

20. J. L. Hoard, W. J. Martin, M. E. Smith, J. F. Whitney, J. Am. Chem. Soc., 76, 3820 (1954).

21. P. A. Kozmin, Zh. Strukt. Khim., 5, 70 (1964).
J. Struct. Chem. (USSR) (Eng. Trnsl.), 5, 60 (1964).

22. D. Grdenič and B. Matovič, Nature, 182, 465 (1958).

23. J. V. Silverton and J. L. Hoard, Inorg. Chem., 2, 243 (1963).

24. D. T. Cromer and A. C. Larson, Acta Cryst., 9, 1015 (1956).

25. J. Singer and D. T. Cromer, Acta Cryst., 12, 719 (1959).

26. A. C. Larson and D. T. Cromer, Acta Cryst., 14, 128 (1961).

27. J. L. Hoard, G. L. Glen, J. V. Silverton, J. Am. Chem. Soc., 83, 4293 (1961).

28. G. L. Glen, J. V. Silverton, J. L. Hoard, Inorg. Chem., 2, 250 (1963).

29. L. Wolf, H. Bärnighausen, Acta Cryst., 13, 778 (1960).

30. R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling and G. B. Robertson, Nature, 192, 222 (1961).

31. S. J. Lippard, F. A. Cotton, P. Legzdins, J. Am. Chem. Soc., 88, 5930 (1966).

32. R. A. Lalancette, M. Cefola, W. C. Hamilton, S. J. LaPlaca, Inorg. Chem., 6, 2127 (1967).

33. F. A. Cotton, J. G. Bergman, J. Am. Chem. Soc., 86, 2941 (1964).

34a. R. Stromberg, C. Brosset, Acta Chem. Scand., 14, 441 (1960).

34b. R. Stromberg, Acta. Chem. Scand., 17, 1563 (1963).

35. J. L. Hoard, E. Willstädter, and J. V. Silverton, J. Am. Chem. Soc., 87, 1610 (1965).

36. H. Bode and G. Teufer, Acta Cryst., 9, 929 (1956).

37. D. B. McWhan and G. Lundgren, Inorg. Chem., 5, 285 (1966).

38. D. L. Kepert, J. Chem. Soc., 1965, 4736.

39. W. H. Zachariasen and H. A. Plettinger, Acta Cryst., 12 (1959).

40. G. A. Barclay, T. M. Sabine and J. C. Taylor, Acta Cryst., 19, 205 (1965).

41. J. H. VanVleck, J. Chem. Phys., 3, 803 (1935).
42. G. E. Kimball, J. Chem. Phys., 8, 188 (1940).
43. M. G. Szirmazan, D. E. Dyatkina, Zh. Fiz. Khim., 27, 491 (1953).
44. G. Racah, J. Chem. Phys., 11, 214 (1943).
45. G. H. Duffey, J. Chem. Phys., 18, 746 (1950).
46. G. H. Duffey, J. Chem. Phys., 18, 1444 (1950).
47. R. V. Parish and P. G. Perkins, J. Chem. Soc. (A), 1967 345.
48. L. Pauling, *The Nature of The Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York (1960) p. 509.
49. R. V. Parish, Op. Cit., p. 453.
50. R. V. Parish, Op. Cit., p. 451.
51. S. J. Lippard, "Eight Coordination Chemistry'' in *Progress in Inorganic Chemistry, Vol 8*, F. A. Cotton, Ed., Interscience, New York, 1967, P. 124
52. H. Stammreich and O. Sala , Z. Electrochem., 64, 741 (1960).
53. H. Stammreich and O. Sala, Z. Electrochem., 65, 149 (1961).
54. E. König, Theoret. Chim. Acta, 1, 23 (1962).
55. R. M. Golding, A. Carrington, Mol. Phys., 5, 377 (1962).
56. J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, J. Am. Chem. Soc., 85, 249 (1963).
57. M. Randić, Croat. Chem. Acta, 32, 189 (1960).
58. G. Gliemann, Theoret. Chim. Acta, 1, 14 (1962).
59. J. H. E. Griffiths, J. Owen, and I. M. Ward, Proc. Roy. Soc., A 219, 526 (1953).
60. J. S. Griffith and L. E. Orgel, Quart. Rev., 11, 381 (1957).
61. M. Randić, J. Chem. Phys., 36, 2094 (1962).
62. J. D. Swalen and J. A. Ibers, J. Chem. Phys., 37, 17 (1962).
63. R. G. Hayes, J. Chem. Phys., 44, 2210 (1966).
64. B. R. McGarvey, Inorg. Chem., 5, 476 (1966).
65. R. V. Parish, Spectrochim. Acta, 22, 1191 (1966).
66. S. F. A. Kettle and R. V. Parish, Spectrochim Acta, 21, 1087 (1965).
68. E. L. Muetterties, Inorg. Chem., 4, 769(1965).
69. E. L. Muetterties and C. M. Wrigt, Quart. Rev., 21, 136,(1967).
70. L. E. Marchi, W. C. Fernelius and J. P. McReynolds J. Am. Chem. Soc., 65, 329 (1943).
71. A. C. Lunn and J. K. Senior, J. Phys. Chem., 33, 1027 (1929).
72. S. J. Lippard, Op cit., p. 136f
73. L. E. Marchi, and J. P. McReynolds, J. Am. Chem. Soc., 65, 333 (1943).
74. F. A. Johnson and E. M. Larsen, Inorg. Chem., 1, 159, 1962.
75. F. A. Cotton, P. Legzdins and S. J. Lippard, J. Chem. Phys., 45, 3461 (1966).
76. H. Bauer, J. Blanc and D. L. Ross, J. Am. Chem. Soc., 86, 5125 (1964).
77. C. Brecher, H. Samelson, and A. Lempicki, J. Chem. Phys., 42, 1081(1965).
78. W. H. Zachariasen, Acta. Cryst, 7, 795 (1954).
78a. C. A. Coulson and A. R. Lester, J. Chem. Soc., 1956, 3650.
79. M. E. Dyatkina and Y. N. Michailov, Zh. Strukt. Khim, 3, 724 (1962).
J. Struct. Chim. (USSR)(Eng. Transl), 3, 701, (1962).
80. K. V. Narasimhan, J. Sci. Ind. Res. (India), 24, 618 (1965).
81. M. E. Dyatkina, V. P. Markov, I. V. Tsarapkina and Y. N. Mikhaildv,
Zh. Neorgan. Khim, 6, 575 (1961)
Russ. J. Inorg. Chem (Eng. Transl), 6, 293 (1961).
82. S. P. McGlynn and J. K. Smith, J. Mol. Spectry., 6, 164 (1961).
83. S. P. McGlynn and J. K. Smith, J. Mol. Spectry., 6, 188, (1961).
84. D. K. Straub, R. S. Drago and J. T. Donoghue, Inorg. Chem., 1, 848 (1962).
85. F. A. Cotton and J. Bergman, J. Am. Chem. Soc., 86, 2941 (1964).
86. C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton and S. C. Wallwork, Proc. Chem. Soc., 1964, 367.
87. J. G. Bergman and F. A. Cotton, Inorg. Chem., 5, 1208 (1966).
88. J. D. Swallen, and J. A. Ibers, J. Chem. Phys., 37, 17 (1962).
89. D. G. Tuck and R. M. Walters, Inorg. Chem. 2, 428 (1963).

METAL-LIGAND BONDING IN SUBSTITUTED METAL CARBONYLS

Wayne P. Anderson April 25, 1968

The nature of the bonding between the metal and the ligands in substituted metal carbonyls has been investigated extensively in recent years.[1,2] By far the most widely used technique has been the study of the infrared frequencies of the carbonyl stretching vibrations as a function of the types of heteroligands present.[3] The results have often been interpreted in terms of the extent of pi bonding between the metal and the heteroligand.[4] Some recent results, however, indicate that changes in the sigma bonding ability of the heteroligand may be the determining factor affecting the carbonyl stretching frequencies.[5-8] Sigma bonding effects must also be considered when interpreting kinetic results.[9]

In order to gain a better understanding of the relative importance of the donor and acceptor properties of various ligands, we have investigated some substituted metal carbonyls by means of infrared intensities and molecular orbital calculations.

Infrared Intensities of Arenechromiumtricarbonyls

The nature of the bonding between the ring and the metal in arenechromiumtricarbonyls is open to dispute. While the net effect of the ring is one of a donor,[10-13] there is evidence which suggests that the ring may also serve as an acceptor in these complexes.[14-15] Cotton and Richardson[16] have suggested that the near equality of metal-carbon bond distances for the M-CO groups of (dien)$Cr(CO)_3$ and $C_6H_6Cr(CO)_3$ implies that there is no backbonding to the ring in the benzene complex. Dobson and Houk[9], on the other hand, attribute the similarity of bond lengths to two competing effects; according to them, backbonding to the ring produces a weaker metal-carbon pi bond and stronger metal-carbon sigma bond in the arene complex, while the greater donor strength of the amine leads to a weaker metal-carbon sigma bond and stronger pi bond in the amine complex.

It has been shown[8] that in compounds of the type $Mo(CO)_5L$, infrared intensities of the carbonyl stretching modes provide an indication of the existence of or non-existence of pi bonding between the metal and the heteroligand. We have measured the intensities of the two infrared-active carbonyl bands in a series of arenechromiumtricarbonyls in an attempt to ascertain whether backbonding to the ring occurs.

Our results indicate that the intensity of the E mode is somewhat dependent upon the nature of the substituents on the ring. It is largest when electron-releasing groups are present and smallest when electron-withdrawing groups are present. The overall change, however, is quite small. The intensity of the A_1 mode, within experimental error, is constant. These results have been interpreted in terms of backbonding to the ring.

Backbonding should be greatest when electron-withdrawing groups are present on the ring and least when electron-releasing groups are present.[15] At the same time, the donor ability of the ring should be greatest when electron-releasing groups are present. Since both of the above effects contribute to the dipole moment derivatives, and therefore the intensities,[17] the net change in intensities is small. If no backbonding occurred, one would expect the intensities of both bands to vary considerably with a change of donor strength of the ring.

Molecular Orbital Theory of Substituted Metal Carbonyls

Molecular orbital calculations have been carried out on chromium hexacarbonyl using two separate approaches.[18-19] An extension of these

methods to a number of substituted metal carbonyls is limited by the great amount of computer time required for large molecules when all of the valence orbitals are included in the basis set. Therefore, a model using a much smaller basis set, but incorporating the important interactions in substituted metal carbonyls, would be useful in determining the effects of various ligands on the electronic structure of these complexes.

A model based on the pi orbitals of the metal and the ligands will be discussed. The pi electrons are assumed to move under the influence of a core Hamiltonian which includes the sigma electronic effects. Several methods of treating sigma effects will be compared. The various approximations will be tested by comparing calculated quantities for substituted metal carbonyls with experimental observables such as force constants, infrared intensities, reaction rates, and stereochemistry of the products.

References

1. T. A. Manuel, Adv. Organometal. Chem., 3, 181 (1965).
2. G. R. Dobson, I. W. Stolz and R. K. Sheline, Adv. Inorg. Chem. Radiochem., 8, 1 (1966).
3. The term " heteroligand" will refer to any ligand bonded to the complex other than carbon monoxide.
4. W. D. Horrocks, Jr., and R. C. Taylor, Inorg. Chem., 2, 723 (1963).
5. M. Bigorgne, J. Inorg. Nucl. Chem., 26, 107 (1964).
6. R. J. Angelici, J. Inorg. Nucl. Chem., 28, 2627 (1966).
7. R. J. Angelici and M. D. Malone, Inorg. Chem., 6, 1731 (1967).
8. D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7, 0000 (1968).
9. G. R. Dobson and L. W. Houk, Inorg. Chim. Acta., 1, 287 (1967).
10. B. Nicholls and M. C. Whiting, J. Chem. Soc., 551 (1959).
11. G. Klopman and F. Calderazzo, Inorg. Chem., 6, 977 (1967).
12. O. L. Carter, A. T. McPhail and G. A. Sim., J. Chem. Soc. (A) 822 (1966).
13. E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, Chem. Ber., 91, 2763 (1958).
14. J. D. Holmes, D. A. K. Jones and R. Pettit, J. Organometal. Chem., 4, 324 (1965).
15. D. A. Brown and H. Sloan, J. Chem. Soc., 3849 (1962).
16. F. A. Cotton and D. C. Richardson, Inorg. Chem., 5, 1851 (1966).
17. $A_i = \frac{N\pi}{3C^2}\left(\frac{\partial\mu}{\partial Q_i}\right)^2$ where A_i is the intensity of the ith normal mode, N is Avogadro's number, and C is the velocity of light.[20]
18. A. F. Schreiner and T. L. Brown, J. Am. Chem. Soc., 90, 0000 (1968).
19. K. Caulton and R. F. Fenske, to be published.
20. J. Overend, "Quantitative Intensity Studies and Dipole Moment Derivatives," in Infrared Spectroscopy and Molecular Structure, M. Davies, Ed., Elsevier Publishing Co., New York, New York, 1963, p. 353.

EXPERIMENTAL AND THEORETICAL STUDIES OF INORGANIC REACTIONS

Steven S. Zumdahl April 30, 1968

I. Nuclear Magnetic Resonance Kinetic Studies

A. Previous Studies

During the past few years nuclear magnetic resonance techniques have become quite valuable in the study of very fast chemical reactions.[1-4] The nmr methods have been of particular use to inorganic chemists who have used them to study a wide variety of ligand exchange reactions of the type

$$ML_n + L^* \rightleftarrows ML_{n-1}L^* + L$$

Most of the investigations on systems of this type have involved octahedral complexes which have been studied in aqueous solution or by using the free ligand as solvent.[5-30] Under these conditions there has been no opportunity to study, definitively, the role of the free ligand in the exchange mechanism. Thus, a primary objective of the present investigation was to study ligand exchange reactions in relatively inert solvents where solvent effects should be minimal and where the concentration of free ligand could be varied.

Also, since very little is known about the kinetics of the reactions of tetrahedral complexes, it was decided to study the exchange reactions of pseudotetrahedral Co(II) complexes. Very recently, Horrocks and coworkers[31-33] have published studies on the exchange reactions of pseudotetrahedral complexes of Co(II), Ni(II) and Fe(II) with substituted phosphines.

Although the complete line-shape technique has been successfully used to study the exchange reactions of dramagnetic complexes,[34-36] the method has never been used to study the reactions of paramagnetic systems. Since the line-shape technique is much more flexible for studying exchange kinetics than the line-width techniques, it was decided to test the feasibility of applying the former method to paramagnetic complexes.

B. Results

1. Introduction

The ligand exchange reactions of CoL_2X_2 complexes, i.e.,

$$CoL_2X_2 + L^* \rightleftarrows CoLL^*X_2 + L$$

have been studied by nmr techniques. The CoL_2X_2 complexes, with L = hexamethylphophoramide (HMPA) and X^- = Cl^- or Br^-, were studied in deuteriochloroform solution by the slow-exchange line-width method.[24] The CoL_2X_2 complex, with L = 2-picoline and X^- = Cl^- was studied in deuterioacetone solution by use of the complete line-shape technique.

2. Line-Width Studies of the $Co(HMPA)_2X_2$ Complexes.

It was observed that the nmr spectra of solutions of the $Co(HMPA)_2X_2$ complexes containing excess HMPA showed separate signals for the coordinated and free ligand protons at low temperatures. Therefore, the slow-exchange line-width technique[24] was used to obtain values of $\frac{1}{\tau_M}$, the pseudo first-order rate constant for the exchange reaction (where τ_M is the mean lifetime

of a ligand in the primary coordination sphere). By studies of solutions containing various concentrations of excess HMPA it was found that $\frac{1}{\tau_M}$ could be represented by the equation:

$$\frac{1}{\tau_M} = K_1 + K_2\,[L].$$

Arrhenius activation energies were obtained for K_1 and K_2 for the chloro and bromo complexes.

3. Complete Line-Shape Study of $Co(2\text{-pic})_2Cl_2$

nmr studies of solutions of $Co(2\text{-pic})_2Cl_2$ containing excess 2-picoline showed that fast-exchange limiting conditions prevail for this system down to -25°C. Below -25°C exchange broadening was found to occur, and the complete line-shape technique was used to study the exchange kinetics in the -25° to -60° temperature region. The line-shape calculations were done by use of a computer program[37] and the input parameters were obtained from studies in the fast-exchange temperature region. Values of $\frac{1}{\tau_M}$ were obtained by using the computer program to fit a calculated nmr spectrum to each experimental spectrum. Studies of solutions containing various concentrations of excess ligand showed that $\frac{1}{\tau_M}$ can be represented by the equation

$\frac{1}{\tau_M} = K_2[L]$. The arrhenius activation energy was obtained for K_2.

C. Discussion

It is interesting to note that the exchange reactions of the two CoL_2X_2 complexes studied here do not follow the same type of rate laws, as might have been expected. The $Co(HMPA)_2X_2$ complexes exhibit mixed first- and second- order kinetics while $Co(2\text{-pic})_2Cl_2$ shows purely second-order kinetics. Horrocks and coworkers[31-33] have found that the substituted phosphine complexes of the type CoL_2X_2, NiL_2X_2 and FeL_2X_2 all exhibit purely second-order exchange kinetics. On the basis of Cortauld atomic models and comparison of the activation energies for K_1 for $Co(HMPA)_2Cl_2$ and $Co(HMPA)_2Br_2$, it appears that the first-order process for the HMPA complexes may be due to a sterically-induced dissociative-type mechanism.

II. Theoretical Studies of the *trans* Influence and *trans* Effect Series

A. Introduction

A great many kinetic studies have been conducted on the substitution reactions of square planar platinum(II) complexes, and it has been found that the ability of a ligand to labilize the *trans* group to substitution decreases in the order[38]

$$C_2H_4 \sim NO \sim CO \sim CN^- > R_3P \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^- > SCN^- > NO_2^- > I^- \cdot$$
$$Br^- > Cl^- > NH_3 > OH^- > H_2O$$

This is the so-called *trans* effect series.[38-40] Most early theories of the *trans* effect emphasized the destabilization of the ground state of the complex by a weakening of the bond *trans* to the *trans* director, L.[41-44] More recent explanations have emphasized the effects of L on the energy of the activated complex for *pi*-[45,46] and *sigma*-[39,40] bonding *trans* directors.

Another phenomenon characteristic of square planar platinum(II) complexes, which deals specifically with the effect of a ligand on the strength of the opposite metal-ligand bond, is called the trans influence phenomenon. The trans influence of ligands has been studied by infrared,[47-54] nuclear magnetic resonance,[56-58] and X-ray[59] techniques and it has been found that the trans influence series is very similar to the trans effect series.

B. Extended Hückel Calculations on Platinum(II) Complexes

In order to explore the theoretical bases for the trans effect and trans influence phenomena, molecular orbital calculations of the extended Hückel type[60] were performed on a series of complexes of the type trans $PtCl_2(L)(NH_3)$, where L represents H_2O, NH_3, Cl^-, H_2S, CH_3^-, PH_3, and H^-.

In order to investigate the relative trans influences of the L groups, the changes in the Pt-N reduced overlap population and overlap energy were studied as L was varied. The results of this study indicate that there is a close parallel between the kinetic trans effect series and the trans influence series, in agreement with the results of the infrared, nmr, and X-ray studies. Further, a study of the changes in the Pt-Cl bond strength as L was varied indicates that a ligand with a high trans influence also has a large cis influence.

The facts that the Pt-N bond weakening in going from a poor to a very effective trans director was observed to be quite small and that the trans and cis influences of a given ligand appear to be about the same, suggest that bond weakening is probably not the primary cause of the kinetic trans effect for sigma-bonding ligands. Rather, our data seem to support the explanation of the trans effect for sigma-bonding ligands given by Gray.[39,40] This explanation is based on the ability of a ligand to stabilize the activated complex for the substitution reaction by interaction with the platinum $6p_6$ orbital. In order to explore the feasibility of this proposal, we have calculated the $Pt(6p_6)$-L overlap populations for the series of ligands mentioned above. The results indicate that there is a rather dramatic increase in the $Pt(6p_6)$-L interaction as L is varied from a poor (H_2O) to a very good (H^-) trans director. Indeed, there is an almost exact correspondence between the ability of L to interact with the $Pt(6p_6)$ orbital and its position in the trans effect series.

Also, extended Hückel calculations were done to estimate the difference to be expected in the activation energies for the substitution reactions of complexes containing a poor trans director (H_2O) and a very effective trans director (H^-). The calculated activation energy difference of 8 kcal/mole agrees quite remarkably with the value of 8-9 kcal/mole expected from the experimental rates of the substitution reactions of complexes containing H_2O and H^-.[40] Also, it was found that the calculated activation energy difference could be traced back almost entirely to the different interactions of these two ligands with the $Pt(6p_6)$ orbital.

Thus, our results strongly support Gray's explanation for the kinetic trans effect of sigma-bonding ligands, although bond weakening effects may also contribute in some cases.

References

1. A. Lowenstein and T. M. Connor, Ber. Bunsenges. Physik. Chem., 67, 280 (1963).
2. R. G. Pearson and M. M. Anderson, Angew. Chem., Intern. Ed. Engl., 4, 281 (1965).
3. J. Delpuech, Bull. Soc. Chim. France, 2697 (1964).
4. T. R. Stengle and C. H. Langford, Coordin. Chem. Rev., 2, 349 (1967).
5. T. J. Swift and R. E. Connick, J. Chem. Phys., 37, 307 (1962).
6. R. G. Pearson and R. D. Lanier, J. Am. Chem. Soc., 86, 765 (1964).
7. J. P. Hunt, H. W. Dodgen, and F. Klanberg, Inorg. Chem., 2, 478 (1963).

8. H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, ibid., 4, 1061 (1965).
9. H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, ibid., 4, 206 (1965).
10. R. B. Jordan, H. W. Dodgen, and J. P. Hunt, ibid., 5, 1906 (1966).
11. Z. Luz and S. Meiboom, J. Chem. Phys., 40, 2686 (1964).
12. Z. Luz, ibid., 41, 1748, 1756 (1964).
13. N. A. Matwiyoff, Inorg. Chem., 5, 788 (1966).
14. N. A. Matwiyoff and S. V. Hooker, ibid., 6, 1127 (1967).
15. D. K. Ravage, T. R. Stengle, and C. H. Langford, ibid., 6, 1252 (1967).
16. J. S. Babiec, Jr., C. H. Langford, and T. R. Stengle, ibid., 5, 1362 (1966).
17. J. F. O'Brien and W. L. Reynolds, ibid., 2110 (1967).
18. J. Reuben and D. Fiat, ibid., 6, 579 (1967).
19. S. Thomas and W. Reynolds, J. Chem. Phys., 46, 4164 (1967).
20. T. J. Swift, T. A. Stephenson, and G. R. Stein, J. Am. Chem. Soc., 89, 1611 (1967
21. J. C. Sheppard and J. L. Burdett, Inorg. Chem., 5, 921 (1966).
22. K. Wüthrich and R. E. Connick, ibid., 6, 583 (1967).
23. T. J. Swift and T. A. Stephenson, ibid., 5, 1100 (1966).
24. Z. Luz and S. Meiboom, J. Chem. Phys., 40, 1058, 1066 (1964).
25. S. Nakamura and S. Meiboom, J. Am. Chem. Soc., 89, 1765 (1967).
26. W. G. Movius and N. A. Matwiyoff, Inorg. Chem., 6, 847 (1967).
27. A. Fratiello, R. Schuster, and D. Miller, Mol. Phys., 11, 597 (1966).
28. A. Fratiello, D. Miller, and R. Schuster, ibid., 12, 111 (1967).
29. A. Fratiello and R. Schuster, J. Phys. Chem., 71, 1948 (1967).
30. R. Schuster and A. Fratiello, J. Chem. Phys., 47, 1554 (1967).
31. W. D. Horrocks, Jr., and L. H. Pignolet, J. Am. Chem. Soc., 88, 5929 (1966).
32. L. H. Pignolet and W. D. Horrocks, Jr., ibid., 90, 922 (1968).
33. L. H. Pignolet, D. Forster, and W. D. Horrocks, Jr., Inorg. Chem., 7, 828 (1968).
34. K. C. Williams and T. L. Brown, J. Am. Chem. Soc., 88, 4134 (1966).
35. L. M. Seitz and T. L. Brown, ibid., 88, 4140 (1966).
36. L. M. Seitz and T. L. Brown, ibid., 89, 1602 (1967).
37. S. S. Zumdahl and R. S. Drago, J. Am. Chem. Soc., 89, 4319 (1967).
38. F. Basolo and R. G. Pearson, Progress in Inorganic Chemistry, Vol. 4, ed. F. A. Cotton, Interscience, New York, 1962, pp 381-453.
39. F. Basolo, "Mechanisms of Inorganic Reactions", Advances in Chemistry Series, ed. R. F. Gould, American Chemical Society, Washington, D.C., 1965, pp 81-106.
40. C. H. Langford and H. B. Gray, Ligand Substitution Processes, W. A. Benjamin, Inc., New York, 1965, pp 18-54.
41. I. I. Chernyaev, Ann. inst. platine (U.S.S.R.), 5, 109 (1927).
42. B. V. Nekrasov, J. Gen. Chem., U.S.S.R., 7, 1594 (1937).
43. A. A. Grinberg, Acta Physicochim. U.R.S.S., 3, 573 (1935).
44. Y. K. Syrkin, Bull. acad. sci., U.R.S.S. Classe sci chim., 69 (1948).
45. J. Chatt, L. A. Duncanson, and L. M. Venanzi, J. Chem. Soc., 4456 (1955).
46. L. E. Orgel, J. Inorg. Nucl. Chem., 2, 137 (1956).
47. J. Chatt, L. A. Duncanson, and L. M. Venanzi, J. Chem. Soc., 4461 (1955).
48. D. B. Powell, ibid., 4495 (1956).
49. J. Chatt, L. A. Duncanson, B. L. Shaw, and L. M. Venanzi, Disc. Far. Soc., 26, 131 (1958).
50. J. Chatt, L. A. Duncanson, and B. L. Shaw, Chem. and Ind., 859 (1958).
51. D. M. Adams, J. Chatt, and B. L. Shaw, J. Chem. Soc., 2047 (1960).
52. D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, ibid., 734 (1964).
53. K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, Inorg. Chem., 4, 36 (1965).
54. J. R. Durig, B. R. Mitchell, D. W. Sink, and J. N. Willis, Jr., Spectrochim. Acta, 23A, 1121 (1967).
56. A. Pidcock, R. E. Richards, and L. M. Venanzi, J. Chem. Soc. (A), 1707 (1966).
57. a. G. W. Parshall, J. Am. Chem. Soc., 86, 5367 (1964).
    b. G. W. Parshall, ibid., 88, 704 (1966).
58. S. O. Grim, R. L. Keiter, and W. McFarlane, Inorg. Chem., 6, 1133 (1967).
59. Reference 38, p. 402.
60. F. A. Cotton and C. B. Harris, Inorg. Chem., 6, 369 (1967).

ASSOCIATION OF SOME ALKYLLITHIUM COMPOUNDS IN HYDROCARBON MEDIA AS A FUNCTION OF ADDED LEWIS BASES

Harlan L. Lewis May 2, 1968

Introduction

The states of aggregation of alkyllithium compounds in hydrocarbon media have been measured by a number of workers[1-13] using colligative property techniques. The published data share the common defect that relatively large uncertainties exist in the results. Thus the extant data are inadequate to determine whether the extent of association varies with concentration or whether it is solvent independent.

Also the effect of added Lewis bases such as ethers and amines on alkyllithium compounds has been examined by several techniques[6,14-18] and states of aggregation and solvation have been reported. Again there is substantial disagreement about both aspects in either mixed or in pure basic media. Most of the data are fragmentary and therefore not amenable to detailed interpretation.

Aggregation in Hydrocarbon Media

We have investigated the extent of aggregation of several alkyllithium compounds in cyclohexane and benzene by cryoscopic measurements. The compounds exist in the two solvents as hexameric aggregates unless steric interference due to branching at either α- or β- carbon becomes significant, in which case they form tetrameric aggregates. Equilibria between these two species are affected by changes in temperature, concentration, and solvent.

Aggregation in the Presence of Basic Substrates

When an ether substrate is added to a hydrocarbon solution of a hexameric alkyllithium, changes in the state of aggregation and solvation occur and are dependent upon base strength and steric size. Although solvated dimers have been proposed as the final state in basic media[14], most evidence supports a solvated tetrameric species[15,17,18] as the only significant product.

We have followed the changes in the nature of the system with colligative property measurements, ^{7}Li nmr, and proton nmr. Both ethyl and n-butyllithium in the presence of excess THF or diethylether are clearly tetrameric, and the extent of solvation is most likely four. The position of the several equilibria at low base to hexamer ratios is not entirely clear.

Utilizing the same techniques, it is apparent that cineole, a bicyclic ether, does not interact with n-butyllithium to an appreciable extent, and with ethyllithium to only a slight extent. Further, both organolithium reagents are probably hexameric in neat cineole.

The data on these two alkyllithium species in the presence of triethylamine do not lead to an unambiguous distinction regarding the nature of the aggregates in neat base. They may be either hexameric or tetrameric, although steric factors favor the latter. In any case, it seems clear that disruption of the organolithium to solvated dimer does not occur in any of the systems studied.

References

1. K. B. Piotrovski and M. P. Ronina, Dokl. Akad. Nauk S.S.S.R., 115, 737 (1957).
2. J. W. Connolly and G. Urry, Inorg. Chem., 2, 645 (1963).
3. M. Weiner, G. Vogel, and R. West, Inorg. Chem., 1, 654 (1962).
4. T. L. Brown, D. W. Dickerhoof and D. A. Bafus, J. Am. Chem. Soc., 84, 1371 (1962).

5. I. Craubner, *Z. Phys. Chem.*, 51, 225 (1966).
6. T. L. Brown, R. L. Gerteis, D. A. Befus, and J. A. Ladd, *J. Am. Chem. Soc.*, 86, 2135 (1964).
7. Fr. Hein and H. Schramm, *Z. Phys. Chem., A*, 151, 234 (1930).
8. T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, 79, 1859 (1957).
9. G. W. Wittig, F. J. Meyer and G. Lange, *Annalen*., 571, 169 (1950).
10. D. Margerison and J. P. Neuport, *Trans. Faraday Soc.*, 59, 2058 (1963).
11. S. Bywater and D. J. Worsfold, *J. Organomet. Chem.*, 10, 1 (1967).
12. G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, 3, 1656 (1964).
13. R. H. Baney and R. J. Krager, *Inorg. Chem.*, 3, 1657 (1964).
14. a. J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, 85, 2171 (1963);
    b. Z. K. Cheema, G. W. Gibson and J. F. Eastham, *ibid*., 85, 3517 (1963);
    c. Z. K. Cheema, G. W. Gibson and J. F. Eastham, *ibid*., 87, 3276 (1965);
    d. Screttas and J. F. Eastham, *ibid*., 88, 5668 (1966);
    e. J. F. Eastham, F. A. Settle, and C. G. Screttas, *Exchg. React., Proc. Symp. Upton, N.Y.*, 1965, 335.
15. a. R. Waack and P. West, *J. Organomet. Chem.*, 5, 188 (1966);
    b. P. West and R. Waack, *J. Am. Chem. Soc.*, 89, 4395 (1967);
    c. R. Waack, M. A. Doran and P. E. Stevenson, *J. Organomet. Chem.*, 3, 481, (1965);
    d. R. Waack, M. A. Doran and P. E. Stevenson, *J. Am. Chem. Soc.*, 88, 2109 (1966)
16. E. A. Kovrižnyx, F. S. Jakušin, and A. J. Šatenštejn, *Reakts. Sposobnost Org. Soedin, Tartu Gos. Univ.*, 3, 209 (1966).
17. L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, 88, 2174 (1966).
18. W. P. Weber, Ph.D. Thesis, Harvard Univ. (1967).

ELECTRON DELOCALIZATION IN PARAMAGNETIC NICKEL(II) - AMMINE COMPLEXES

Ronald J. Fitzgerald May 7, 1968

Introduction

Since the classic study of the esr spectrum of $[IrCl_6]^{2-}$ by Griffiths and Owen[1] in 1954-from which they deduced that the unpaired electron spends 70% of its time in iridium 4d orbitals and 5% of its time on each chlorine nucleus - a vast amount of physical evidence has accumulated indicating covalency in the metal-ligand bond.

The first recognized example of nmr contact shifts was observed in 1957 by McConnell and Holm[2] who studied solid, paramagnetic nickelocene. Since that time both esr and nmr have been used extensively to study the delocalization of unpaired electron spins.

We have investigated electron delocalization in a series of nickel(II)-ammine complexes using nmr contact shifts. This is a particularly cogent choice of complexes as will be shown later.

As Orgel[3] has pointed out, " If we want to find out about covalency... we should determine the electron density in the molecule very accurately." Thus, experimental work of this nature has provided a great impetus to theoreticians doing " quantitative" molecular orbital calculations.

Following an early attempt by Wolfsberg and Helmholz[4] to calculate energies and intensities of electronic transitions in XO_4^{n-} ions, a calculation[5] of the energy levels of $[VO(H_2O)_5]^{2+}$, which appeared to be remarkably successful, has led to the expenditure of considerable effort to devise and test schemes of calculating molecular orbital energy level diagrams.

We have used an Extended Hückel Theory[6] (EHT) molecular orbital treatment in an attempt to correlate the calculated spin densities with the experimental spin densities in some nickel(II)-ammine complexes.

Experimental Results

Many authors[7,8,9,10] have taken the delocalization of unpaired electron density into the π-orbitals of conjugated ligands as evidence of metal-ligand π-bonding. However, alternative explanations[11] have been offered and we decided to investigate the nmr contact shifts of $[Ni(bz)_6]^{2+}$ (bz = benzylamine) to determine whether unpaired electron spin can be delocalized into the π-orbitals even though the metal-ligand bond is primarily σ.

We isolated a light blue complex with the formula $[Ni(bz)_5BF_4]$ (BF_4).[11] On the basis of conductance, spectral, and magnetic data, we believe the octahedral complex $[Ni(bz)_6]^{2+}$ is formed in solutions of nitromethane containing excess benzylamine.

Since octahedral nickel(II) complexes are of cubic symmetry and possess a $^3A_{2g}$ ground state, the g tensor should be isotropic and there should be no pseudo-contact interaction.[12] Thus, we can consider the observed contact shifts to be isotropic and interpret them in terms of spin delocalization mechanisms.

Our nmr results[11] show that the distribution of spin densities at the phenyl protons is that expected for a π-delocalization mechanism, even though the metal-ligand bond is σ.

Our contact shift results may be interpreted by assuming a mechanism[13,14] that operates in the reverse of one that has been used to explain the hyperfine coupling of π-electrons in the phenyl ring with methylene or methyl protons for a series of organic radicals. In this mechanism, a pseudo π-orbital[13] interacts directly with the phenyl ring.

Although there have been several studies[15,16] in which σ delocalization mechanisms have been reported to be the dominant mechanisms, the majority of previous contact shift work has been concerned with delocalization of unpaired spin in π-systems. In most of the systems studied previously, the ligands were complex and it has often been difficult to sort out σ and π contributions to the delocalization mechanisms. Consequently, we chose these relatively simple alkyl amine ligands to evaluate delocalization in a σ molecular orbital.

Our nmr results[17] indicate that a σ delocalization mechanism is dominant in the alkyl chain in the octahedral complexes[18] $[Ni(R\text{-}NH_2)_6]^{2+}$ ($R = CH_3$, C_2H_5, n - C_3H_7). The large upfield shift of the amino protons, in all the complexes studied, indicatesthat a spin polarization mechanism is dominant here. This has recently been discussed[19] in terms of competition between opposing mechanisms.

Molecular Orbital Calculations

The Extended Hückel Theory calculations were carried out on the ligand by a previously described method,[20] incorporating subsequent modifications.[21,22]

The unpaired spin density at different protons was evaluated using a ψ^2 program that has been described previously[21].

In σ systems, the experimentally determined hyperfine coupling constants are related to the spin densities by a simple equation[23]. Thus, using the ratio of hyperfine coupling constants, we may obtain experimental ratios of spin densities to compare with our calculated results.

Although we found that rotation about the N-C, C_3 bond axis does not affect the spin densities in methylamine , the spin densities of ethylamine were found to be extremely sensitive to rotation about the N-C, C_3 bond axis.

From study of a Courtauld Atomic Model of $[Ni(C_2H_5NH_2)_6]^{2+}$, we decided that only three configurations of this complex would be stable. A 0°,0° rotamer and configurations corresponding to rotations about the N-C bond, from 0°,0° or staggered, staggered to ± 70° (with an error of ± 5°). We found that when the probability of existence of the less sterically hindered 0°,0° rotamer is two and a half times as great as that of the ± 70° rotamers , a good fit is obtained for the ratio of the methyl and methylene hyperfine coupling constants in the ethylamine complex. A check on the reasonableness of the assumptions for ethylamine is provided by calculating the ratio $CH_2(C_2H_5NH_2)/CH_3(CH_3NH_2)$. The excellent agreement in this final calculated ratio lends credibility to our previous estimates.

Bibliography

1. J. H. E. Griffiths and J. Owen, Proc. Roy. Soc. (A), 226, 96 (1954).
2. H. M. McConnell and C. H. Holm, J. Chem. Phys., 27, 314 (1957).
3. L. E. Orgel in "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1960, p. 114.
4. M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20, 837 (1952).
5. C. J. Ballhausen and H. Gray, Inorg. Chem., 1, 111 (1962).
6. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).
7. D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, J. Chem. Phys., 37, 347 (1962).
8. G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, J. Chem. Phys., 41, 2126 (1964).
9. F. A. LaLancette and D. R. Eaton, J. Am. Chem. Soc., 86, 5145 (1964).
10. R. W. Kluiber and W. D. Horrocks, Jr., Inorg. Chem., 5, 152 (1966).

11. R. J. Fitzgerald and R. S. Drago, J. Am. Chem. Soc., 89, 2879 (1967).
12. H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361 (1958).
13. D. H. Levy, Mol. Phys., 10, 233 (1966).
14. J. P. Copla and E. DeBoer, Mol. Phys., 7, 333 (1963-1964).
15. J. Happe and R. L. Ward, J. Chem. Phys., 39, 1211 (1963).
16. D. R. Eaton, A. D. Josey, and R. E. Benson, J. Am. Chem. Soc., 89, 4040 (1967).
17. R. J. Fitzgerald and R. S. Drago, J. Am. Chem. Soc., 90, 0000 (1968).
18. R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, Inorg. Chem., 2, 1056 (1963).
19. B. B. Wayland and W. L. Rice, Inorg. Chem., 6, 2270 (1967).
20. P. C. Van der Voorn and R. S. Drago, J. Am. Chem. Soc., 88, 3255 (1966).
21. R. S. Drago and H. Petersen, Jr., J. Am. Chem. Soc., 89, 3978 (1967).
22. G. Burns, J. Chem. Phys., 41, 152 (1964).
23. R. S. Drago and H. Petersen, Jr., J. Am. Chem. Soc., 89, 5774 (1967).

COORDINATION OF MOLECULAR NITROGEN

David J. Brauer May 14, 1968

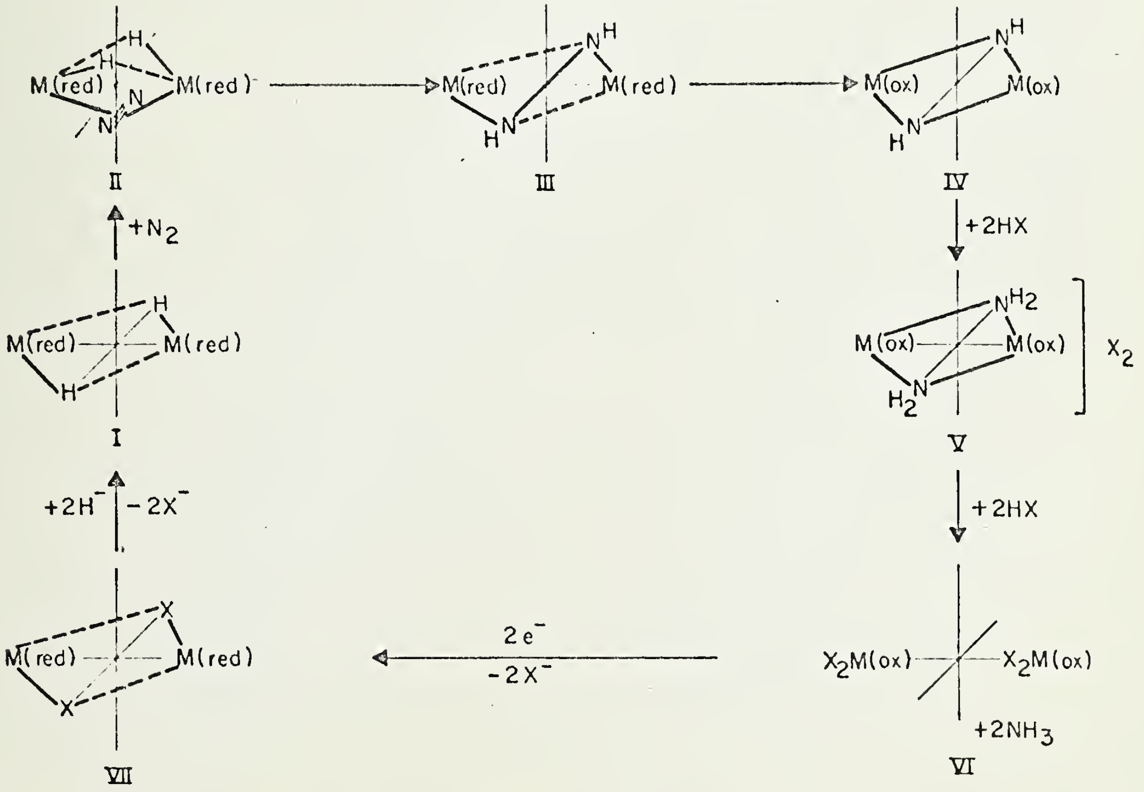
Introduction

Containing one of the strongest chemical bonds, nitrogen is difficult to oxidize or reduce. In fact, it is used as an inert gas in many chemical systems. Although the only successful process for producing ammonia industrially requires the treatment of a mixture of nitrogen and hydrogen with catalysts under high pressures and elevated temperatures, bacteria have long been known to be able to produce ammonia at normal temperatures and pressures.

In the past few years a number of systems have been found which not only produce ammonia from nitrogen, but also contain molecular nitrogen as a ligand. The efforts to find a means for the catalytic production of ammonia have spurred interest in the study of complexes in which molecular nitrogen is a ligand. It is the purpose of this seminar to relate the preparation of ammonia to these complexes and to describe the properties of these complexes with respect not only to the coordination of nitrogen but also to their application to chemical synthesis.

Ammonia Producing Systems

Certain solutions which contain transition metal compounds and organometallic reagents and which have been treated with gaseous nitrogen liberate ammonia on hydrolysis. It has been difficult to understand how the nitrogen molecule can pick up six equivalents of charge in the formation of ammonia since the source and mechanism of the electron exchange is difficult to determine. Early workers believed that in these reactions the hydrogenation of nitrogen is facilitated by the presence of hydrogen in the reagent or solvent molecules.[1] It has been shown that in some systems the treatment of the fixing solution with hydrogen gas before introduction of nitrogen enhances the yield of ammonia.[2] The $(C_5H_5)_2TiCl_2$ (I)-$(C_2H_5)_2O$ (II) system, a particularly good nitrogen fixation system, has been studied extensively. Brintzinger has postulated a mechanism for this fixation (Fig. 1),



(M(red) = metal in reduced state; M(ox) = metal in oxidized state; HX = acidic reagent)

Figure 1

which is based on ESR[3] data. Treating the conversion to ammonia essentially as an insertion of the nitrogen molecule into metal hydride bonds, he has postulated a mechanism which would make possible a smooth transition from molecular nitrogen to ammonia by facilitating the transfer of electrons to the nitrogen *via* hydride ions. At the same time the formation of unfavorable intermediates such as diimines is prevented by converting the nitrogen molecule into two bridging groups.[4] On the other hand, studies by Russian workers using $(C_5D_5)_2TiCl_2$ and C_2D_5MgBr in $(C_2D_5)_2O$ have shown that the ammonia formed upon hydration with undeuterated acids was not deuterated. They postulated that a transient intermediate, which fixed the nitrogen as nitrides, was formed by a reaction between I and II while hydrogenation took place only during the hydrolysis step.[5] Brintzinger's mechanism has also been challenged on the basis of kinetic data. British workers report that I and II react vigorously to form an intermediate of unknown structure, stable over a period of hours, which is able to fix nitrogen. They also postulate that the nitrogen is fixed as nitride and propose the mechanism below:

(1) $2[Ti(C_5H_6)_2] + C_2H_2MgBr = [Ti_2(C_5H_6)_4]$

(2) $[Ti_2(C_5H_6)_4] + N_2 = [(C_5H_6)_2TiN]$ 1 or 2 .

where (1) is the rate determining step at high nitrogen pressures and (2) is the rate determining step at low nitrogen pressures.[6]

Complexes with Coordinated N_2

Allen and Senoff's $[Ru(NH_3)_5N_2]X_2$ (III) compounds ($X=Cl$, Br, I, BF_4, PF_4) were the first complexes discovered in which N_2 is coordinated to a transition metal. They were prepared by adding $N_2H_4(H_2O)$ to an aqueous solution of $RuCl_3$. The salt precipitated from solution upon addition of a saturated, aqueous solution of the appropriate anion.[7] The complexes have been characterized by analysis, conductivity, magnetic suseptability, IR, NMR, and X-ray crystallography. In each case the compounds were found to be 2:1 electrolytes in $(CH_3)_2SO$ and diamagnetic. The IR showed a strong, sharp peak in the region 2105-2170 cm^{-1}, which has been assigned to the N-N stretch. NMR data showed no high field peak which would indicate the presence of a hydride. Upon heating, they obtained N_2 of high purity. Upon treatment of the complex with 20% $NaBH_4$ or 40% NaOH, 5.93 ± .07 moles of NH_3, instead of the expected 7.0 moles, were obtained per mole of complex.[8] The crystal and molecular structure of the chloride salt of III indicated that the RuN_2 part of the complex is nearly linear, but disorder in the crystal made it impossible to determine the Ru-N (of N_2) and N-N bond distances.[9] Allen and Senoff's compound III has been prepared in many different ways, including the following:

(1) $RuCl_3OH + Zn + N_2 = III^{10}$

(2) $[Ru(NH_3)_5H_2O](CH_3SO_3)_3 + NaN_3 = III^{8}$

(3) $[Ru(NH_3)_5Cl]Cl_2 + H_2SO_4 + Zn + \text{air} = III^{11}$

(4) $RuCl_3 + Zn + NH_3(\text{aqueous or anhydrous}) = III^{12}$

(5) $[Ru(NH_3)_5H_2O]^{2+} + N_2 + H_2SO_4 = III^{13}$.

Japanese workers have isolated complexes reported to be $[Co(PPh_3)_3N_2]$[14,15] and $[Co(PPh_3)_3N_2H]$[15]. The number of hydride hydrogens present in these compounds has been questioned. Italian chemists have reported the following reaction:

$$[Co(PPh_3)_3H_3] + N_2 = [Co(PPh_3)_3N_2H] + H_2.$$

They have shown that the resulting compound gives off two moles of N_2 per mole of H_2.[17] For each of these compounds, an IR band at 2088 cm^{-1} has been assigned to the N-N stretch. Ibers and coworkers have reported the crystal and molecular structure of $[Co(PPH_3)_3N_2H]$. They concluded that the hydride ion could be present, but unfortunately decomposition of the crystal in the X-ray beam prevented conclusive determination. The Co-N distance is 1.80 ± .04Å; the N-N distance is 1.16 ± .04Å. They also found two IR bands at 2085 and 2105 cm^{-1}, and they assigned these peaks to the Co-H and N-N stretch respectively.[18]

Some other N_2 containing complexes have been described. A series of compounds $[Os(NH_3)_5N_2]X_2$ (X = Cl, Br, I, ClO_4, BF_4, and BPh_4) (V) have been made in the same way that III was originally prepared.[19] Taube and coworkers have synthesized the binuclear complex $\{[Ru(NH_3)_5]_2N_2\}(BF_4)_4$. The fact that there is no sharp IR band in the region 2000-2200 cm^{-1}, but rather only a broad band in this region, indicates that the N_2 may be a symmetrically bonded bridging group.[20] Collman and coworkers have prepared $[Ir(PPh)_3N_2Cl]$ (VI) by reacting organic azides, such as furoyl azide, with Vaska's compound.[21,22] Using $[Rh(PPh_3)_2(CO)Cl]$ and butyric acid azide, Russian workers have prepared $[Rh(PPh_3)_2N_2Cl]$.[23]

Reactions of N_2 Complexes

Molecular nitrogen complexes have been shown to undergo substitution and oxidation reactions. The complex III has been useful in forming several compounds which are otherwise difficult to prepare such as: $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5(CH_3)_2SO)]I_2$, $[Ru(NH_3)_4(C_5H_5N)_2]I_2$, and $[Ru(NH_3)_2(C_5H_5N)_4](BF_4)_2$.[8] The osmium complex (V) has greatly simplified the formation of $(Os(NH_3)_5I)I_2$, which was previously difficult to prepare.[19] The complex $[Co(PPh_3)_3N_2H]$ can undergo reversible exchange with H_2 and C_2H_4, the N_2 being the leaving group.[24] Collman's complex VI reacts with various isocyanates to form complexes in which a heteronuclear multiple bond, $>C=N-$, is pi bonded to the metal.[21]

Bonding in N_2 Complexes

The aspects of bonding of N_2 to transition metals has not been extensively studied; however, some remarks can be made. That the Ru-N_2 entity can be formed by many different routes indicates a surprising thermodynamic stability for this group.[12] On the other hand, the substitution reactions with H_2, C_2H_4, and isocyanates indicate chemical lability. The formation of the Ru-N_2 entity from atmospheric N_2 indicates that the latter is an effective nucleophile even in competition with oxidation by O_2. The fact that the percent of N_2 evolved from Ru-N_2 complexes never reaches 100% also indicates that the N_2-metal bond is strong. Although the stretching frequency of uncoordinated N_2 is 2331 cm^{-1}, the stretching frequency of coordinated N_2 ranges from 2010 -2195 cm^{-1}. This drop in the stretching frequency is analogous to that of the carbonyl complexes. Since N_2 is a poorer base than CO, d(pi)-p(pi) back bonding may be even more important in these complexes. Additional support for a strong back bonding interaction comes from the fact that the rocking vibrations of the NH_3 groups in III occur in the frequency range of $[Ru(NH_3)_6]X_3$ and $[Ru(NH_3)_5X]X_2$ rather than in the lower frequency range of the $[Ru(NH_3)_6]X_2$ NH_3 rocking mode, a fact which indicates that the compound III has a higher effective charge than does the analogous $[Ru(NH_3)_6]X_2$ (X = Cl, Br, I).[8,25]

Conclusion

In the study of the coordination of molecular nitrogen, the primary goals are the designing of a homogeneous catalyst system for the production of ammonia and the elucidating of the biological processes of nitrogen fixation. Although stable, molecular nitrogen coordinated transition metal complexes have been shown to be useful in providing easier routes for the synthesis of certain transition metal complexes, much work needs to be done to explain why, in certain systems, molecular nitrogen-metal bonds are so easily formed.

Bibliography

1. M. E. Vol'pin and V. B. Shur, DAN, 156, 1102 (1964).
2. M. E. Vol'pin, Ilatovskaya, Larikov, Khidekel, Shvetsov, and Shur, Dokl. Chem., 164, 861 (1965).
3. H. Brintzinger, J. Am. Chem. Soc., 88, 4305, 4307 (1966).
4. H. Brintzinger, Biochem., 5, 3947 (1966).
5. G. N. Nechiporenko, G. M. Tabrina, A. K. Shilova, and A. E. Shilov, Dokl. Chem., 164, 977 (1965).
6. R. Maskill and J. M. Pratt, Chem. Commun., 950 (1967).
7. A. D. Allen and C. V. Senoff, ibid., 621, (1965).
8. A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, J. Am. Chem. Soc., 89, 5597 (1967).
9. F. Bottomley and S. C. Nyburg, Chem. Commun., 897 (1966).
10. A. E. Shilov, A. K. Shilova, and Yu. G. Borod'ko, Kinetika i Kataliz, 7, 768 (1966).
11. A. D. Allen and F. Bottomley, Can. J. Chem., 46, 469 (1968).
12. J. Chatt and J. E. Fergusson, Chem. Commun., 126 (1968).
13. D. F. Harrison and H. Taube, J. Am. Chem. Soc., 89, 5706 (1967).
14. A. Yamamoto, S. Kitasume, L. S. Pu, and S. Ikeda, Chem. Commun., 79 (1967).
15. A. Misono, Y. Uchida, and T. Saito, Bull. Chem. Soc. Japan, 40, 700 (1967).
16. A. Misono, Y. Uchida, T. Saito, and K. M. Song, Chem. Commun., 419 (1967).
17. A. Sacco and M. Rossi, ibid., 316 (1967).
18. J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, ibid., 96 (1968).
19. A. D. Allen and J. R. Stevens, ibid., 1147 (1967).
20. D. F. Harrison, E. Weissberger, and H. Taube, Science, 159, 321 (1968).
21. J. P. Collman, M. Kubota, J. Y. Sun, and F. Vastine, J. Am. Chem. Soc., 89, 169 (1967).
22. J. P. Collman and J. W. Kang, ibid., 88, 3459 (1966).
23. L. Yu. Ukhin, Yu. A. Shvetsov, and M. L. Khidekel, Izv. Akad. Nauk. S.S.S.R., Ser. Khim., 4, 957 (1967).
24. A. Yamamoto, L. S. Pu, S. Kitasume, and S. Ikeda, J. Am. Chem. Soc., 89, 3071 (1967).
25. A. D. Allen and C. V. Senoff, Can. J. Chem., 45, 1337 (1967).

UNIVERSITY OF ILLINOIS-URBANA
546IL6I C001
INORGANIC SEMINAR ABSTRACTS URBANA
1967/66
3 0112 025503100